PB86-184744

Control of Organic Substances in Water and Wastewater

Massachusetts Univ., Amherst

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Apr 83

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/8-83-011	2.	3. RECIPIENT'S ACCESSION NO. PB86 184744/AS
4. TITLE AND SUBTITLE CONTROL OF ORGANIC SUBSTANCES IN WATER AND WASTEWATER		5. REPORT DATE April 1983 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Bernard B. Berger		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Professor Bernard B. Berger Department of Civil Engineering University of Massachusetts Amherst, MA 01003		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. C2397NASX
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Oh 45268		13. TYPE OF REPORT AND PERIOD COVERED Project Report/Summary 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The presence of organic substances of industrial origin in wastewaters, storm runoff and in surface and groundwaters may not always be an unmitigated evil--but, it is safe to say, it never is good. In 1976, EPA was required to give special emphasis to 129 "priority pollutants" that present probable hazard in the water resource. Of these 129 priority pollutants, 114 are organic.

This document is comprised of 14 chapters, each prepared by a specialist. Chapter 1, Fundamental Considerations in the Removal of Organic Substances in Water is in essence an examination of a wide spectrum of physical chemical principles that are being used, are under study, or may in the future be adapted for use in the separation of organic pollutants in waters.

Chapters 2, 3, 4, and 5 reveiw the status of techniques for the separation of destruction of organic imppurities in drinking water. Chapters 6, 7, 8 and 9 review current methods, old and new, and assess their potential role in the future control of the priority organic pollutants contained in municipal wastewaters. Chapters 10, 11, 12, 13 and 14 examine existing and proposed new methods for control of organic substances in industrial wastewaters.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Wastewater Organic Substances Priority Pollutants Industrial Wastewater Municiapl Wastewater	Biological Treatment Adsorption Recycling Air Stripping	

18. DISTRIBUTION STATEMENT UNLIMITED	19. SECURITY CLASS *(This Report)* NONE	21. NO. OF PAGES 480
	20. SECURITY CLASS *(This page)* NONE	22. PRICE

United States
Environmental Protection
Agency

EPA-600/8-83-011
April 1983

PB86-184744

Research and Development

EPA

Control of Organic Substances in Water and Wastewater

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/8-83-011
April 1983

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FOREWORD

The formation of the U.S. Environmental Protection Agency in 1970 ushered in the first decade of environmental awareness as a total national phenomenon. It was a decade punctuated by major Congressional mandates to restore the nation's waters, to reduce air pollution, and to find a comprehensive approach to other environmental problems—those associated with pesticide use, hazardous waste disposal and toxic substances. It was a decade underscored by the demand for new technology and better science to answer environmental questions and to solve environmental problems.

As the scientific and technical arm of the Agency, The Office of Research and Development is responsible for advancing the state of knowledge about the environment such that critical issues and questions can be addressed and answered effectively, based on the application of state-of-the-art science and technology. In the years since 1970, The Office of Research and Development has produced manifold increases in the data base from which environmental decisions are made and in the sophistication of the understanding which has provided the basis for decisions.

This volume represents our effort to take stock of scientific advances in research pertaining to organic substances since the inception of the Agency and to gauge what progress has been made and what remains to be accomplished. The essays in this volume present a range of perspectives on the subject, from the vantage points of the scientific and technical disciplines which have been carrying out relevant research. The points of view represented are varied and sometimes conflicting. But scientific progress depends on just such diversity. The authors at times have speculated about emerging problems and research needs. Such attempts require extrapolation based upon informed scientific judgment. The outcome of that process must, in the final analysis, be recognized as opinion and not fact.

PREFACE

INTRODUCTION

The presence of organic substances of industrial origin in wastewaters, storm runoff and in surface and groundwaters may not always be an unmitigated evil--but, it is safe to say, it never is good. Our concern is not new. Reports of federal efforts to identify and contend with such pollutants go back 30 years. In the last decade, and with good reason, this fear has flared up. In 1976, EPA was required to give special emphasis to 129 "priority pollutants" that present probable hazard in the water resource. Of these 129 priority pollutants, 114 are organics. The number will surely be increased with additional knowledge and experience.

We have made a national commitment to eliminate or reduce these priority organic pollutants. But it is difficult and costly to do so, and before we can proceed effectively, we must have additional information concerning these substances. First, of course, we must know they are indeed present; it is hard to take protective action against a specific organic compound whose presence is not known or even suspected. This is important, but by itself it is not enough. We must know what maximum concentration of that substance may be tolerated. Such information gives point and purpose to our approach to control. And then we must have the technology to effect the reduction. Each "we must....." represents a challenge to those engaged in water and wastewater research.

Detection of the presence of a hazardous pollutant in water or municipal wastewater may result simply from knowledge of its use in the community or on land. Its presence in industrial wastewaters may be a logical deduction from knowledge of materials contributed by the industrial plant. Maintaining such intelligence is a routine but important activity of pollution control agencies. Knowledge so gained must be supplemented by information obtained by actual examination of the process waters and plant discharges.

Unfortunately, knowledge derived from plant discharge monitoring may not be complete. This is particularly true if the pollutant gives no physical, chemical or biological clue to its presence. We became aware of this problem in the early 1950's when municipal wastewater treatment plants throughout the nation generated enormous, even dramatic, quantities of foam. This was quickly traced to the alkyl benzene sulfonate (ABS) component of household detergent which had only recently been placed on the market. There was no difficulty in identifying ABS; the physical evidence was clear to the point of gross nuisance. The ABS episode stimulated us to ask what other chemical pollutants might be present that unlike ABS were not detectable and that conceivably might be much more important from the standpoint of public health.

Detecting and measuring the unknown pollutant is one major challenge. Here we look to the chemists. Another is determining the effect of the pollutant, and based on this, recommending a tolerable concentration in the effluent and water resource. For this information we look to our co-workers in epidemiology, toxicology and in the ecologic sciences. Their conclusions present a third and major challenge to the engineer: developing procedures for treating water and wastewater to meet stringent requirements for water quality. This document is a status report on how this challenge is being met.

The document is comprised of 14 chapters, each prepared by a specialist. Chapter 1, Fundamental Considerations in the Removal of Organic Substances in Water is in essence an examination of a wide spectrum of physical chemical principles that are being used, are under study, or may in the future be adapted for use in the separation of organic pollutants in waters.

Chapters 2, 3, 4, and 5 review the status of techniques for the separation or destruction of organic impurities in drinking water. Chapter 2, Coagulation-Sedimentation-Filtration Processes for Removing Organic Substances from Drinking Water, assesses the state-of-the-art for the long used, conventional processes in respect to the new challenges posed by organic pollutants in general and trihalomethanes in particular, and discusses ways in which the full potential utility of these processes may be employed. Chapter 3, Adsorption of Organic Substances in Drinking Water, reviews the theory of adsorption phenomena, experience in the use of adsorption in removal of trace organics in drinking water, and problems still to be overcome in assuring maximum efficiency of the process in water purification. Chapter 4, Removal of Organic Substances from Water by Air Stripping, describes the theory of gas exchange, analyzes recent experience in air stripping as a treatment process for drinking water, and shows how this process may be efficiently designed to remove trace organics in the raw water. Chapter 5, Oxidation of Organic Substances in Drinking Water, reviews the theory of chemical oxidation and assesses the potential of a number of oxidation processes, alone and in combination with UV, in the destruction or modification of organic pollutants present in drinking water in trace concentrations.

Chapters 6, 7, 8 and 9 review current methods, old and new, and assess their potential role in the future control of the priority organic pollutants contained in municipal wastewaters. Chapter 6, Reduction of Organic Substances in Municipal Wastewater by Biological Processes, examines long familiar processes from a new perspective which provides a deeper understanding of basic physical-chemical and microbiological phenomena, and in so doing, shows how such processes, including their latest adaptations, may be employed most efficiently in removing priority organic pollutants. Chapter 7, Reduction of Organic Substances in Municipal Wastewaters by Physical-Chemical Processes, describes experience in the USA with such processes, including recent applications and the future potential based on this experience, and focuses on the theory and applications of adsorption as that physical-chemical principal having the greatest potential in removing trace priority pollutants. Chapter 8, Treatment of Municipal Wastewaters for Recycle/Reuse, discusses current policy and practices, obstacles to be overcome, particularly those presented by trace organic compounds, and the probable future role of reclamation of municipal effluents. Chapter 9, Management of Organic Residuals Separated from Municipal Wastewaters, describes the probable behavior and fate of trace priority organic pollutants in sewage, a difficult and uncertain effort because of very scanty data, and discusses possible interactions between such pollutants and processes of sewage sludge conditioning and treatment for disposal.

Chapters 10, 11, 12, 13 and 14 examine existing and proposed new methods for control of organic substances in industrial wastewaters. Chapter 10, Reduction of Organics in Industrial Wastewaters by Biological Treatment, represents a thorough review of experience with existing biological treatment systems, evaluates the potential effectiveness of such systems in controlling trace organics, and describes design and operating factors that will improve treatment efficiency. Chapter 11, Removal of Organic Compounds from Industrial Wastewaters Using Adsorption Processes With Activated Carbon, reviews industrial experience in use of adsorption focusing particularly on practical design and operational factors for adsorption and carbon regeneration systems. Chapter 12, Separation of Organic Substances in Industrial Wastewaters by Membrane Processes, presents a timely analysis of the state-of-the-art, problems still to be solved, and the probable future role of membrane processes in controlling trace organic substances in industrial effluents.

Chapter 13, Treatment of Industrial Wastewaters for Recycle/Reuse, discusses the potential role of such recycle/reuse in reclaiming industrial wastewaters, describing recent experience, the problems to be solved, proposed approaches to such recycle/reuse, and the substantial advantages to industry in reclamation of wastewater. Chapter 14, Management of Organic Residuals Separated from Industrial Wastewaters, describes the character and quantity of residuals produced by various industrial categories, and the methods recommended in handling, treating and disposing of these residuals.

The foregoing chapters focus on the priority organic pollutants that are known to us, on ways to make maximum efficient use of our treatment technologies, and on new processes that may be used in the future. It is evident, of course, that new problems resulting from generation and wide use of the organic products of industrial operations will surely emerge during the decade to come. Many will be similar to those we now experience. Others will challenge our perceptivity, our foresight and our judgment. The research now underway should help in meeting the tasks of the future. The status report represented by this MONOGRAPH could well be viewed as an audit of 1980 concepts in contending with synthetic organic pollutants. They tend to indicate, also, the probable technologies of the future.

Bernard B. Berger
Technical Editor

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FUNDAMENTAL CONSIDERATIONS IN THE REMOVAL OF ORGANIC SUBSTANCES FROM WATER - A GENERAL OVERVIEW

Louis Koenig, PhD

INTRODUCTION

The Nation has become increasingly aware of the importance of water cleansing processes. Enormous sums are spent on wastewater treatment works and municipal plants for the treatment of drinking water. These processes, once mysterious--even arcane--to the general public, are now described in books available even to school children. Most are now familiar with the conventional terminology—grit removal, clarifiers, trickling filters, activated sludge, sludge digestion, coagulation and flocculation, settling, filtration and disinfection.

Ironically, at a time when the public has shown it has a general appreciation of works designed to separate pollutants from water and has expressed its willingness to approve huge appropriations for that purpose, it learns that many potentially dangerous pollutants are not in fact removed. The bulk of these pollutants, organic chemicals of industrial origin, are, in a sense, new to nature.

It is appropriate and timely that we re-examine the pollutant separation processes, not in terms of efficiency, as important as this surely is, but rather to assess our understanding of the fundamental physical, chemical and biochemical mechanisms involved. More than that, we should extend our inquiry to identify principles to be potentially applied in meeting the challenges presented by the new, often complex, synthetic organic chemicals reaching our water resources. A preliminary re-examination is the objective of this chapter.

THE STATES OF AGGREGATION OF ORGANICS IN WATER

Organics in water may be in dissolved, suspended, settled, or floating states. Organic substances that are not dissolved in water can exist in solid, liquid or gaseous phases as either continuous or disperse.

If an organic gas exists in a continuous phase, its lower surface must be the upper surface of the liquid. Thus, the organic substance is already separated from the water. The same is true if the organic substance is in a continuous liquid phase which differs in density from that of water.

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Organics as a Disperse Phase

In the disperse phase, particles are separated from each other and surrounded by water molecules. The particles may be solid, liquid, or gas.

Dispersions are classified according to particle size, the size being thought of as the diameter of a sphere of the volume equal to the volume of the particle. The classification distinguishes between coarse dispersions and colloidal dispersions or colloids. The properties which distinguish colloids from coarse dispersions are particle size and surface area. Since these properties vary continuously with those parameters, there cannot be a precise boundary between the classes.

Colloidal Particles—

The properties peculiar to colloidal particles become evident at particle sizes below 500 nanometers (nm, 10^{-9} meters), which is about the lower limit of visibility with a standard microscope; thus, colloidal particles cannot be studied effectively with a standard microscope but only with the ultramicroscope, an instrument which passes a beam of light through the dispersion and observes the particles by means of the flashes of light reflected from them. Such an instrument can detect particles of about 5 nanometers (10^{-9} meters), the approximate diameter of some complex molecules of high molecular weight such as proteins and starches which exhibit colloidal properties even though the "particles" are single molecules. The size of 5 nanometers is therefore used to define the boundary betwen colloidal materials and true solutions.

So far we have presented colloidal particles as simple spheres; however, the forms that colloids actually take are more complicated and this affects their properties. For individual, or primary, particles, the shape may be spherical, ellipsoidal, plate-like or rod-like, or filamentous.

An aggregation of many simple particles may also be referred to as a particle. The forces which hold the aggregate together are either coulombic, arising from net positive or negative charges on the primary particles or "van der Waals" forces. Coulombic forces may be either attractive or repulsive, their magnitude decreasing with the square of the distance between the particles. The van der Waals forces are generated by a shifting of the electrical charges within the neutral particle so as to concentrate the positive charge toward one end of the particle and the negative to the other, a phenomenon called polarization. In this way, attractive forces occur between particles. The magnitude of the attraction decreases with the cube of the distance, and therefore van der Waals forces are generally significant only at very small distances between particles.

It is obvious that such aggregation increases the diversity of particle sizes so much that it may make suspensions out of colloids, again one of the mechanisms for separation of organics.

A third modification to the simple spherical particle concept is that of hydration, a phenomenon in which molecules of water become associated with a colloidal particle. Some of this water may be tightly bound around the surface of the particle in a layer about one molecule thick. Frequently, larger quantities of water molecules are associated, but these are more loosely bound than the initial layer and may be merely entrapped in the coils and folds of an aggregate particle. This association of water molecules increases the volume of the particle and thus the diameter, but it also makes the specific gravity of the particle closer to that of the water in which it is suspended. Since the difference in density between the particle and the water is important for settling and floating, the extent of hydration becomes important in the separation of the particles from the water phase.

Adsorbed Organics—

Organics have thus far been discussed as if they were the only materials in the dispersed phase. However, if inorganic particulates are present, they may adsorb organic molecules or particles. Conversely, the organic particulates might aggregate not only with other organic molecules and particulates but also with inorganic particulates. This is important because physical separation techniques that depend only on particle size--sedimetation, for example--remove both the organics and the inorganics. Furthermore, some of the removal techniques involve adding inorganic particulates to adsorb the organics and make them amenable to removal.

The Embodiments of the Physical States

Table 1, shows the physical states in which organics occur in water as a disperse phase and the corresponding embodiment for solutions. The continuous phase, that is the dispersing medium, is, of course, the water solution. The table shows that organic solids, liquids, and gases can occur as coarse suspensions, or as colloids, in which case the names applied are sols, emulsions, and foams. Most emulsions have particle sizes in the upper portion of the colloid range. There is no special terminology for the coarse suspensions. Also, organic compounds which, in the pure state, are solids, liquids or gases can occur as solutes under ambient conditions in the water phase. In this case, they are liquids in the sense of being part of the homogeneous liquid phases and have lost their characteristics as solids or gases.

THE CHEMICAL NATURE OF ORGANICS

The distinction between organic compounds produced by the cellular processes of living organisms and organic compounds produced by man in factory or laboratory becomes important in the subject we are addressing. Before the development of the chemical manufacturing industry, all organic compounds in natural waters and in wastes reaching them did come from the cellular processes of living organisms. Other organisms evolved which were adapted to utilizing these compounds in their own metabolic processes, excreting in turn simpler compounds with the eventual end products being inorganic compounds such as carbon dioxide and water. By such adaptation, certain organisms, especially the microorganisms, served to remove organic compounds from soils and waters, and, with respect to the latter, provide purification. Hence, they were harnessed by man under artificial conditions to do so, as in sewage treatment plants.

In the past half century, the situation has become complicated because a host of synthetic organic compounds has been produced. These compounds differ from those which certain organisms had adapted to metabolizing. Indeed, some of the manufactured compounds, e.g. the pesticides, have been produced specifically to thwart the established metabolic processes. These new products, termed "exotics," thus defy conventional treatment processes. They pass through conventional treatment plants unchanged and are termed "refractory," "recalcitrant," "biorefractory," and "non-biodegradable," the latter two terms reflecting the dominance of biological processes in man's approach to the problem.

The Multiplicity of Organic Compounds

An advanced textbook intended for the education of organic chemists easily indexes 4000 compounds. And that, as with all textbooks, is only the beginning. Chemical Abstracts has in its file some 4,600,000 organic compounds which have been mentioned in the literature since 1965, to be added to the 1,200,000 which were already prepared or identified before 1965 but not yet filed. And the file is being expanded at the rate of about 330,000 per year.

The number of organic compounds that can theoretically exist is obviously enormous. For example, among the paraffin hydrocarbons, compounds of carbon and hydrogen only, CH_4, methane, C_2H_6, ethane, those with 20 carbon atoms in the

Table 1. The Physical States in Which Organics Occur in Water

	Coarse Suspensions	Colloids	Solute
Number of phases	More than one	More than one	One
Particle size, nm	Greater than 200-500	200-500	Less than 10
Physical states			
Solid	X	Sols	Liquid
Liquid	X	Emulsions	Liquid
Gas	X	Foams	Liquid

molecule number approximately 366,000 possible compounds or about 3.5 million, if one counts stereoisomers, compounds of the same structure but with different spatial orientations among the parts. Among the simple aliphatic alcohols such as methyl CH_3OH and ethyl C_2H_5OH, there are 5.6 million compounds possible with 20 carbon atoms, and 82 million if stereoisomers are counted.

The Classes of Organic Compounds

Some general classes of organic compounds differ in their roles as pollutants. These classes are distinguished by their essential carbon-carbon bonds.

In *aliphatic* compounds, the carbons or other elements are linked in either linear or branched simple chains. Some are saturated (i.e., each carbon is linked to its adjacent carbon by a single valence bond). Others are unsaturated (i.e., the carbon bonds are double or triple). The unsaturated carbon double or triple bond is more easily attacked by chemical reagents than is the single bond. In *alicyclic* (nonaromatic) compounds, the carbon chains have closed upon themselves forming a ring structure. *Heterocyclic* (nonaromatic) compounds, contain an element other than carbon in the ring. *Aromatic* compounds are ring compounds that have special properties. In most, the ring is made of carbons, with a particular linkage of alternating single and double bonds, but heterocyclic compounds may also be aromatic. The closure of the ring in this manner produces, despite the double bond, a structure that is very stable against attack.

Of course, large molecules that occur as organic pollutants in water may be composed of several of the foregoing types of structures, and so may have the properties of the aliphatics at one end of the molecule and of aromatics at the other end.

Many aromatic compounds are toxic or carcinogenic. Two particular classes that are prominent in current environmental literature are polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs).

And finally while describing compounds of major current concern, one should include the trihalomethanes (THMs). These are aliphatic compounds composed of methane, CH_4, in which three of the hydrogens have been replaced with a halogen, the most common being chlorine, producing chloroform, $CHCl_3$.

"Natural and Unnatural" Compounds

The reason for this sketchy introduction to organic compounds is to emphasize that by far the greater part of the Earth's mass of living matter is in the form of aliphatics than in the form of cyclics or aromatics. The bulk of living substance consists of proteins (made up of amino acids), carbohydrates, and fats, all of which are aliphatics. The non-aromatic compounds, alicyclic and heterocyclic, occur in much smaller amounts, and are typically found in the minor components of living organisms including bark, nuts, essential oils, pigments, hormones, and vitamins.

The aromatics are even more rare and are found in living organisms in much smaller amounts in the form of hydroxybenzene, phenol, cresol and relatives in the tannins, lignins, resins, gums and balsams of vegetable material.

Because of the amount and ubiquity of natural aliphatics the organisms adapted to "cleaning-up" the natural environment are well suited to handling this class of compounds; they are less well adapted to metabolizing cyclic compounds, aromatic or non-aromatic.

Organic compounds occur not only in living organisms but also in such fossilized remains as coal and petroleum. In these materials, which have made such an impact on our environment, aromatic compounds occur more frequently and more plentifully.

In the sweep of evolution, therefore, one sees the development of communities of organisms adapted to use (and thus destroy) the organic metabolic products and wastes of other organisms; this symbiosis is highly effective for aliphatic compounds, but much less so for the largely refractory aromatics and other cyclics. However, a rather felicitous order in nature has been put in disarray. We are now producing large quantities of aromatics from fossil materials that previously were not available; more than that, we are now synthesizing organic compounds, aromatics and others, never before known to nature. These materials are often released in concentrated form, overwhelming nature's defensive mechanism. The immense challenge their control presents cannot be exaggerated. With this view it is interesting to recognize that among the organics and pesticides listed by EPA as priority pollutants most are aromatics and most of the residue of non-aromatics are aliphatic compounds which are found nowhere in nature. Many of the latter are more resistant to destruction than the aromatics.

THE ORGANICS IN WATER AND WASTEWATER

It is reasonable to assume that an examination of organics removed will contain some description of the specific organic compounds and their concentration actually found in water and wastewater. However, a mere mention will have to suffice; to list the organics found in water and wastewaters would require all of the remaining pages of this monograph. Over 1300 have been identified in the United States. Even in treated drinking waters, supposedly largely free of organic matter present in the water source, about 300 synthetic organic compounds have been found occurring in two or more systems. Thousands of organic compounds may be found in single-celled microorganisms routinely recovered from wastewaters. Many more will surely be identified in the future.

Organics in Natural Waters

While most of the unresolved problems associated with organics in waters are man-induced, the notion that "natural" waters, that is, waters untouched by man, are "pure" has long since been dispelled. When the Advanced Waste Treatment Program was being established by the U.S. Public Health Service in 1960, an effort was made to set the maximum allowable concentration goal for nitrogen compounds at a low value. However, that goal was abandoned when it was pointed out that water in a pristine headwater stream running over the granite in the remote regions of the Rocky Mountains had a nitrogen content higher than that goal.

Indeed, compared with some of the goals being set today, even rainwater before reaching the ground may be contaminated. The organics in some rains studied throughout the world typically lie in the span 5 mg/L to 25 mg/L.

The unpolluted surface waters and groundwaters in North America show organic concentrations averaging about 8 mg/L, and the estuaries about 12 mg/L. However, a survey of the water supplies of 80 cities conducted in connection with the search for trihalomethanes showed the median organic concentration of raw water supplies to be about 1.0 mg/L for ground water and about 6 mg/L for surface water.

The organics in natural unpolluted waters are derived from the products and degradation of plant materials in and on the soil. The major types of compounds are "humic materials," tannins, lignins, phenolics, amino acids, hydrocarbons, and fatty acids. The humic materials are currently of particular interest because of their reported role as the major precursors of trihalomethanes upon chlorination.

It is not uncommon that after organic compounds produced by industrial processes are found to be toxic or carcinogenic, intensified research stimulated by that revelation shows that these compounds may also be produced by natural processes. For example, the source of PAHs, especially benzo(a)pyrene (B(a)P), which was found to be carcinogenic was first attributed to industrial high temperature processing; however, further research revealed that significant amounts of PAHs and specifically B(a)P were produced by bacteria, algae and plants.

Organics in Drinking Water

As already stated, some 300 organic compounds have been identified in the drinking waters being supplied to United States consumers at present. Water, if contaminated, is subjected to appropriate treatment; the finished water has generally been found to meet the established criteria. These criteria and the prescribed treatment methods had been largely concerned with (1) obvious nuisance materials, (2) turbidity, (3) pathogenic organisms, (4) color, (5) taste and odor, and (6) certain chemicals associated with public health hazard. The last comprised for the most part the inorganic impurities. Thus, in the sequence of drinking water standards promulgated passim between the issuance of the initial U.S. Treasury Drinking Water Standards in 1914 and the National Interim Primary Drinking Water Regulations called for by the 1974 Safe Drinking Water Act, little attention was given to the organic compounds present which while present in small concentrations would be consumed over long periods.

Three movements over the past two decades account for the current interest in residual organics in drinking water and for organics in waters in general. These are: (1) increased capability to identify and measure small concentrations of organics, (2) increased public awareness of environmental threats, and (3) increased concern over chronic effects associated with repeated exposures to low concentration of contaminants over prolonged periods.

The main stimulus for the study of organics in drinking waters came from the discovery in 1974 of chloroform and other trihalomethanes (THMs) in the New Orleans drinking water. Since chloroform is alleged to be carcinogenic the EPA responded with a prompt, widespread and penetrating investigation of the occurrence of such compounds in other drinking waters and of the causes and remedies for the threat. Because THMs were not present in the raw waters it was reasoned that they must be produced in the treatment processes; these were soon narrowed down to the commonly practiced chlorination disinfection process. The chlorine, reacting with organic precursors in the raw water, mostly the humic materials, produced THMs, mostly chloroform.

Organics in Municipal Wastewaters

Not only are organic compounds many and diverse but also the waters and wastewaters bearing them are many and diverse in their organic makeup. Typical characteristics of municipal sewage are presented in Tables 2 and 3. It should be recognized that the compositions vary from day to day and from city to city and therefore the values are to be taken as only rough averages.

Table 2. Concentrations of Organics in Municipal Sewage

Strong	600mg/L*
Median	350mg/L
Weak	175mg/L

* mg/L = milligrams per liter, equivalent to parts per million by weight.

Table 3. Distribution of Organics (in %) in Municipal Sewage According to Size Fractions

Not dissolved	63	Non-filterable	51	Settleable or floating	30
				Not settleable	21
		Colloidal	12		12
Dissolved	37		37		37
Total organics	100		100		100

Table 2 shows that the strength of sewage, measured as total organic matter concentration, varies over at least a four-fold range and is some hundred-fold greater than the organics in natural waters.

Table 3 shows how the organics are distributed among the various size fractions. The non-filterable is that retained on a laboratory filter paper, the not settleable being that portion of it that will not settle or rise in one hour. One worker distinguished between these as settleable meaning settleable or floatable, and supracolloidal (larger than colloidal) which he measured by centrifuging. Note that only about one-third of the organics are in the dissolved state and about one-half are retained on a laboratory filter.

Among the three major groups of organics in sewage the fats comprise about 10% and the remainder is split about equally between proteins and carbohydrates. Other compounds contribute only a few percent at the most to the total organic matter, but may be important as pollutants.

The importance of these distinctions is that with two-thirds of the organics in the nondissolved phase, efficiency in removal requires attention to the removal of particulates. Since such removal methods operate via the physical properties of the particles, they cannot distinguish between the organics and the inorganics (except via gross differences, e.g. settling out the dense inorganics while floating off the less dense organics). Thus processes of this kind for removing the organics also have to handle the inorganics. Furthermore the inorganics may either enhance or hinder the removal of the organics.

The subject should not be left without a reminder that the major components--the proteins, carbohydrates, and fats--are relatively easy to remove by processes historically known and applied; but normal municipal sewage will also contain small amounts of such exotic chemicals as detergents, waxes, insecticides, and other household chemicals. It is these components that may be harmful to man and ecosystems and more difficult to remove. These components of sewage are, however, the products of industry and as previously stated, their sheer multiplicity precludes any overview of them here.

Organics in Industrial Wastewaters

The problem of industrial wastewaters has been intensified by the enormous growth of the petrochemical industries and their ancillary chemical industries. Their products pervade our society and reach our waters either directly through discharges from industrial plants or indirectly through consumer discharges to municipal sewers or on land.

We have learned to cope with such traditional industrial wastes as those from food processing, textile manufacture, pulp and paper manufacture, pharmaceuticals manufacture, the metal industries, and conventional chemical plants. The best available technology appears adequate for handling wastewaters from these industries.

The challenge we face comes primarily, but not solely, from the synthetic organic chemicals. This challenge has been defined in terms of specific priority pollutants or families of pollutants that are of special concern because of feared carcinogenic, mutagenic or teratogenic effects. Every industrial plant producing wastes containing these pollutants must meet stringent requirements for waste treatment whether the plant effluent is discharged to the receiving water or the municipal sewer. Development of ways to separate these difficult pollutants is a major task facing science and engineering.

PHYSICAL MECHANISMS FOR THE REMOVAL OF ORGANICS

The two general approaches to removing organics from water are to destroy them or to move them somewhere else. The first involves chemical transformations of the organic substances, the essential process being a cleavage of the chemical bonds in the organic molecule. This may be accomplished by electrical forces, heat, or chemical agents either added as such or generated in the water phase by radiation or electrical means. The necessary action is that the molecule change into one or more other molecules. It is most desirable that the new molecules not themselves be organics; the ultimate objective is complete destruction and removal of organics by the transformation into CO_2, H_2O, nitrogen and other easily removed or harmless inorganic substances. Less desirable is the transformation of the original organics into organics of lower molecular weight which are generally more easily removed and have lesser potential for harm than the original compounds. This does not represent destruction of the organics, because for every original molecule one or more different molecules, also organic, are produced. However, this is still removal of the original molecule species and can be a desirable goal, such as the breaking up of a toxic molecule into small non-toxic molecules.

The second approach uses physical forces to move pollutants from the main water phase to another location where they can be separated from the main water body. The physical forces used may include a quasi-chemical bonding, for example, adsorption on surfaces. Also, to be effective, the physical force used may have to be preceded by a chemical reaction, for example, one that changes a soluble organic compound to an insoluble solid that precipitates and can be removed by physical means. But the essential step is a displacement from the main water phase.

Fugacity and Activity

Fugacity and activity are thermodynamic properties involved in a number of mechanisms for removing organics from water. Fugacity measures the escaping tendency, i.e. the tendency to relocate, and activity measures the tendency to enter into chemical reactions.

In a closed system of a water layer (phase) and a gas layer (phase), if a small amount of a volatile organic compound is injected into the water, the concentration of the organic will be high in the water phase and zero in the gas phase. However, the molecules of the organic solute are in random motion in the liquid and some of these random motions propel them through the water surface into the gas phase. The number of molecules per second passing into the gas will be proportional to their concentration in the water phase. But as the molecules build up in the gas phase, they are also in motion, and some of them pass back through the surface into the water phase. The rate at which these do so is also proportional to their concentration in the gas phase. Thus, the concentration in the water phase will decrease and that in the gas phase will increase until the number per second passing out of the water equals the number per second passing out of the gas. Thereafter, no further changes in concentration or in net transport will occur. The system is said to be in equilibrium, sometimes expanded to dynamic equilibrium, which refers to the exchange transport that is still going on.

The molecules of the gas and water and the organic compound that are in the gas phase are so far apart that each species acts as if the others were not present. The total pressure in the gas is the sum of the separate pressures of the separate species, and these separate pressures, called partial pressures, are proportional to the concentration of the particular molecule species. That being so, the partial pressure becomes a measure of the concentration.

In the water phase, the molecules which are much closer together interfere with each other's movements. Consequently their velocities are lower than the velocities in the gas phase. For that reason, the concentration in molecules per cubic centimeter at equilibrium has to be much greater than that in the gas phase, but, as indicated, the rate of passage through the surface is proportional to the concentration.

When that concentration is expressed in terms of mol fraction (i.e. the ratio of the number of moles of compound to the number of moles of water and other compounds in the water phase), then it is found that for any given compound the partial pressure in the gas phase is proportional to the mol fraction in the water phase. This is called Raoult's Law.

The same mechanism, namely the equalization of the rates of transfer in the two directions, applies even if there is no boundary. For instance if a dye is injected at one point into a body of water, it will distribute itself throughout the body until the concentrations are the same everywhere.

Such an explanation would be made by a kineticist (a physical chemist who studies the rates at which processes occur and who therefore thinks of events in terms of rates). His fellow physical chemist, the thermodynamicist, thinks of events, or more properly of conditions, in terms of energy.

There is a thermodynamic property of systems called "free energy." Any spontaneous change occurring in a system does so in such a direction that the free energy (content) of the system decreases. When a system is at equilibrium the free energy content is at a minimum; therefore, all systems not at equilibrium and not under any external force move in the direction of equilibrium, that is toward a lower free energy state and never in the opposite direction. Thus in the dye example the free energy, per mole of dye, in the concentrated dye injected is greater than that in the bulk of the solution. The dye moves so as to decrease its free energy, that is, from the concentrated portion toward the dilute portion and never in the opposite direction.

Thermodynamicists have developed a body of knowledge by which free energies can be calculated from concentrations or pressures, and this is extremely useful in predicting in which direction a process will proceed and how far it will go. But it has been found that these relations hold only in dilute solutions and at low gas pressures. When they are applied at higher concentrations or pressures they do not give the correct answers.

One of the giants of physical chemistry, G.N. Lewis, proposed around 1900 a means to handle this divergency which is immensely useful and widely applicable, although it sounds like a trick. Lewis created an ideal pressure called fugacity and a corresponding ideal concentration called activity which had magnitudes such as to make the thermodynamic equations for free energy give the correct answers when they were substituted for the actual pressures and concentrations. Fugacity measures the escaping tendency, i.e. the tendency to relocate. Activity measures the tendency to engage in chemical reactions.

As fugacity and activity are companion entities, it was necessary to invent fugacity coefficients and activity coefficients, which are the ratios of the fugacity or the activity to the pressure or the concentration. These, as well as the fugacity and activity, vary with pressure and concentration. Again this simple trick made possible the correlation of a wide number of properties and processes and a prediction of the behavior of systems, including prediction of the freezing points and boiling points of solutions, the solubilities of substances, the electromotive force (voltage) of electrical cell reactions, the rate and extent of chemical reactions, the direction of physical and chemical changes, and the distribution of components at equilibrium, e.g., the partial vapor pressures over solutions. As to the latter the law is that at equilibrium the activities, or the fugacities, in the various phases are equal and systems will react so as to attain that condition.

So far this discussion of fugacity has dealt with bulk bodies and surfaces. A surprising fact resulting from free energy considerations is that the fugacity of substances in small bodies is greater than in large. Thus, the fugacity in droplets is greater than in the bulk liquid, and the free energy is in fact inversely proportional to the diameter of the droplet. Therefore, the escaping tendency in small droplets is greater than in large ones, and material from small droplets will be transferred to the larger ones even without any contact or coalescence. For the same reason, the escaping tendency is greater for finely divided solids than for coarse grains, and as a result the solubility of finely ground solids is greater than that of coarse grains; the vapor pressure is also greater.

Because most of the organics in water occur in finely divided form, including as solute molecules, such considerations are of importance in an understanding of the removal of organics and in developing or improving processes for doing so.

Because free energy and fugacity are involved in and control all transport separation processes, even those based on gravitational, centrifugal, magnetic and electrical mechanisms, and chemical change processes, they are particularly applicable to processes that the chemical engineer would call mass transfer processes.

Physical Relocation Concepts

Several distinctions must be made in a logical system for organizing the concepts involved in separation by physical motion.

First, distinction must be made between motion in general and the more specific form that directly results in separation. There are motions experienced by molecules and particles that are either random, undirected, or compensated; in neither case does bulk mass transfer in any particular direction occur. Examples on the microscale are the thermal motions of molecules and the Brownian motions of particles resulting from these random movements of molecules. An example on the macroscale is thermal convection in which bulk transfer occurs upwards in response to the lower density but is exactly counterbalanced by a corresponding downward flow. For want of a better term, we use "relocation" as excluding motions which do not result in gross mass transfer toward a target. We exclude the nondirected motions from the concept of relocation, but we are aware of the fact that such motions still contribute to the ultimate relocation. They do so in ways to be described subsequently.

Secondly, a distinction must be made between directed motion on a macroscale and that on a microscale. The motion of a charged ion or particle toward the oppositely charged surface of an adsorbent is not random, since there is a net displacement toward the adsorbent whether it be fixed in place, as in a packed column, or mobile in the liquid in the form of an added coagulant. In that sense, such motion is not among the random undirected motions excluded earlier. However, with the mobile adsorbents, such motion does not immediately result in physical separation, since that occurs only when the mobile adsorbent is itself separated from the liquid by some subsequent mechanism.

The Driving Forces and Mechanisms In Physical Relocation

The mechanisms that are operative in relocation of solids in water are:

- Gravity
- Centrifugation
- Magnetism
- Surface Tension
  - Foam Fractionation
  - Froth Flotation
- Solvent Extraction
- Stripping
- Distillation
- Osmosis
- Reverse Osmosis
- Adsorption
- Electrokinetics
  - Electrophoresis
  - Electroosmosis
  - Electrodialysis
- Freezing
- Hydration
- Filtration
- Microfiltration
- Flocculation and Sedimentation

Forces classed as macro are those in which the driving force operates at a distance from the target location and the motion occurs over a long pathway; those identified as micro are forces in which the object and the target have to be close together and the motion occurs over only a short pathway. It is obvious that any force that operates on the macroscale must also operate on the microscale. There follows a description of each of the forces or mechanisms listed.

Gravity—

Gravity, the gravitational force between the earth and body near its surface, pulls downward both the liquid and the particle immersed in it with a force proportional to their respective weights, i.e. densities. Since natural systems tend toward the condition of lowest energy state the result is that the dense bodies gravitate to the bottom, the light bodies to the top.

Centrifugation—

Centrifugation is a force quite similar to gravity in its effect but brought about by rotation of the liquid to generate a force outward along the radius of rotation. This may be done by rotating a vessel holding the liquid or by causing the liquid to flow in a circular path in a fixed vessel.

Magnetism—

Magnetism is that force exerted on a material by a magnetic field. All substances experience a force in a magnetic field, a paramagnetic material being drawn to a magnet, a diamagnetic one being repelled from the magnet. Most materials experience only very small forces in a magnetic field but a special class of paramagnetics, called ferromagnetic, experiences forces 10^6 to 10^8 times greater. Thus, though organic substances are not magnetic, finely divided ferromagnetic substances can be added, which, adsorbing the organics or being adsorbed or bound in them, allow the separation by a magnetic field.

Surface Tension—

Surface tension is a force existing at the interface between a liquid and another liquid, a solid, or a gas. It exists because while the molecules in the body of the liquid are fully surrounded by other molecules and thus attracted equally in all directions, those on the surface are attracted only in the direction of the bulk of the liquid. As a consequence the surface tends to contract to the smallest possible area. In order to extend the surface it is necessary to bring a molecule to the surface against the inward force. This work is measured as a force, dynes per centimeter, and the force required to pull the surface apart on a line one centimeter long is called the surface tension. Because of surface tension, liquids that wet a solid experience a force driving them into small pores of the solid, the force being proportional to the surface tension and inversely proportional to the radius of the pore. Thus a blotter, a solid body having small pores, will, against the force of gravity, soak up water which wets it.

In the other direction, if the liquid does not wet the solid a force is experienced which in effect keeps the liquid out of the pores. Thus by proper choice of solid, one may separate wetting liquids from non-wetting liquids, for example, water from oils. Solids wetted by water are called hydrophilic; those not wetted by water are called hydrophobic.

These phenomena are identified as capillary and absorption, and the liquid penetrating the pores is said to be absorbed. This is to be distinguished from the phenomenon of adsorption to be discussed. Absorption is an effect associated primarily with the surface properties of the liquid. Adsorption is associated with the surface properties of the solid.

Certain organic compounds have properties that cause them to preferentially accumulate at water-air or water-solid interfaces. Their attraction for each other and for the water molcules is much weaker than the attraction of water molecules for each other. Also the chemical grouping at one end of the molecule may be attracted to water and at the other end repelled. As a result forces are created that produce a concentration of the compound at the water-air surface or at the water-solid surface. Because its presence reduces the interfacial tension of the water, it is termed a surface active agent. The surface activity of soap and detergents, which are surface active agents, is responsible for their detergency and their foaming tendency.

Foam fractionation—is a process that takes advantage of the foaming tendency as a means of removing surface active agents from water. Since they move to a surface, it follows that their concentration at the surface of a submerged bubble (of air) is greater than in the bulk of the liquid, and that when such bubbles become airborne (i.e. a foam), the ratio of compound to water in the foam will be greater than in the bulk liquid. This is the basis of foam fractionation in which a foam is artificially produced and removed, carrying the surface active agents with it.

Froth flotation—is also based on interfacial tension and is related to but should not be confused with foam fractionation. Froth flotation has been extensively studied and applied in the separation of the constituents of ores. It is used to separate particulate matter, not dissolved matter. When the surface of a particle suspension or colloid is hydrophobic, i.e. repelled by water, the particle will attach itself to the air-water interface of a bubble and will float to the surface. Since most natural minerals have a hydrophilic surface it is the function of an added "collector" to make the hydrophobic surface. The actual molecular operation is amazingly selective. It has been extensively studied but is still a subject of controversy. To confound the picture, secondary additives, called conditioners, can promote or inhibit collection. Those that promote collection are called activators. Whether they act by altering the surface of the particle or by influencing the action of the collector is also a matter of controversy.

Solvent Extraction—

Solvent extraction is a process in which the water is contacted with an immiscible liquid solvent. The organic to be removed is more soluble in the solvent than in the water, that is, its fugacity in the water phase is greater than in the solvent phase, so the escaping tendency is from the water to the solvent until equilibrium is reached. The organic compound of interest transfers from the water to the solvent until the fugacities are equal in the two phases.

Solvent extraction is usually carried out in the sense just indicated, namely, the solute is extracted by the solvent. However, it is quite possible that organic pollutants are very insoluble in the solvent and that the water is very soluble in the solvent. In that case the water would transfer to the solvent phase and the organic pollutants would remain. A considerable amount of experimental research and ingenious theoretical research on this mechanism employing physical-organic electronic theory and the quantum theory of valence was carried out under the Saline Water Conversion Program. It appears that the extraction effect, i.e. the transfer of the water, as well as the selection effect, i.e. the rejection of the solute, depends on groups in the solvent molecule capable of hydrogen bonding, i.e. of the water. Whether this rationale would also apply in the case of organic compounds, which themselves have bondable hydrogen, is an intriguing theoretical and experimental question.

By solvent extraction one ordinarily means extraction of the solute. No special name has been coined for solvent extraction of the water.

Stripping—

Stripping is a process in which the water is contacted with a gas, air being the obvious choice. The more volatile (higher fugacity) organic contaminants transfer to the air phase and are removed.

Distillation—

Distillation is a process for removing organics that are much less volatile than water. Clearly, from the standpoint of thermodynamics, if more volatile compounds can be removed from water by being transferred to the air by stripping, then water can be removed from the less volatile substances by the same means. Distillation is a version of stripping in which the water vapor itself, rather than added air, is the carrier. However, in order to transfer water into the vapor and transport it to the condenser, it is necessary to heat the water. While much of the heat can be recovered, the efficiency of heat transfer and utilization is low, with the result that large amounts of heat are required, and for that reason this process is impractical for removing organics on the scale involved.

Osmosis—

Osmosis is a process in which the driving force also results from a difference in fugacities, that between water and a solution. In the description of the diffusion of a dye into the bulk of a water body only the escaping tendency of the dye, that is, the tendency to move from more concentrated regions to the less concentrated regions, was mentioned. However, a strict reading of the laws shows that in that case the water also moves from the region where it is more concentrated (i.e. the bulk of the liquid), to that region where it is less concentrated (i.e. the injected dye element). The mol fraction of water in the original water is 1.0 and that in the injected dye element is less than 1.0. Thus both the water and the solute will relocate until the fugacity of solute, and also of water, is the same throughout.

If the dye element is separated from the water body by a membrane that allows the passage of water but not of dye, then the water will pass through the membrane but the dye cannot although it has the escaping tendency to do so. Therefore, the water side of the membrane retains its original fugacity and continues to move indefinitely into the dye side until the fugacity (of the water) is the same on the dye side as on the water side (i.e. to infinite dilution). Now, however, if the dye side is a confined space, the incoming water will cause the liquid level on the dye side to rise, thus creating a pressure difference. The process continues until the pressure increases the fugacity of the water on the dye side to the point at which it just equals the fugacity of the water on the water side. Such a membrane is called an osmotic membrane, the process, osmosis, and the pressure difference between the two sides at equilibrium, the osmotic pressure.

Reverse Osmosis—

Reverse osmosis involves an external pressure (on the dye side) equal to the osmotic pressure. With any further increase in the applied pressure, a movement of water will occur in the reverse direction, from the concentrated side to the dilute side. Reverse osmosis is now a commercial process for water purification.

Of interest is that when reverse osmosis was first proposed, as a saline water conversion process about 30 years ago, the general scientific and engineering community gave it a low priority and little chance for success, dubbing it almost a laboratory curiosity. One reason was that process engineers are often repelled by high pressure proposals because of the expensive equipment and the energy required to compress materials. However, most high pressure processing is carried out with gases and the concept of high energy requirements comes from that technology. The fact is that the energy required to raise the pressure on a material is proportional to the pressure times the change in volume. Gases undergo a great change in volume with an increase in pressure, so both terms in the multiplication are large and consequently the energy requirement is large. However, water is highly incompressible, that is, it undergoes only a small change in volume with pressure; therefore, the volume change factor is small and the energy requirement is not so great as it would first appear to be.

A second obstacle to early acceptance of reverse osmosis was the fact that the original membranes did not transfer water at rates that made the process economical. Furthermore, the molecular mechanism by which the water was transferred in either direction had been under dispute for decades and there seemed to be no rationale by which this property could be improved. Fortunately, by a combination of legerdemain, dogged scientific experimentation, and pure luck, two young men in California developed a membrane that had good transfer properties. This showed the way to widespread investigation and improvement of the molecular process.

Adsorption—

Adsorption is the process by which molecules or particles in the liquid or gas phase become attached to a solid. In adsorption, the thermodynamic driving force is the difference in free energy, in activity, between material dissolved or suspended in a liquid and material attached to the surface of a solid. The solid is called the adsorbent, the attached material, the adsorbate.

In general, the whole surface of the adsorbent is not active in the attachment. Some spots are more strongly attractive than others. The theory of adsorption, described in later chapters, therefore involves the number, strength, and distribution of these active spots. The actual forces involved are electrostatic bonding, covalent bonding, or van der Waals bonding. In electrostatic bonding the adsorbed particle bears a net electrical charge, either positive or negative and is attracted to and held at a spot on the surface of the adsorbent which bears the opposite local net charge. Since excess electrons are mobile on continuous surfaces, such localized net excess of electrons does not often occur. A covalent bond is one in which pairs of electrons are shared between two atoms, thus completing the shells of the atom. The van der Waals bond arises as essentially an electrostatic attraction between objects, molecules, particles, or surfaces in which there is no net excess or deficiency of electrons. Instead, the electrons in one or both are mobile so that a positive charge on an adsorbent attracts the electrons in a particle thus building up an excess on the side of the particle facing the adsorbent. Since these electrons are closer to the adsorbent than the positive charges on the other side, the net effect is an overall attraction. The range of effectiveness in attraction is of the order of two molecular diameters.

Adsorption through van der Waals forces is called physical adsorption, distinguishing it from adsorption through covalent bonding, which is called chemisorption. Physical adsorption is accompanied by a heat production called the heat of adsorption, which is 5 to 10 kilocalories (kcal) per mole adsorbed. Chemisorption, a stronger bond, has a heat of adsorption of 10 to 100 kcal/mole. In some cases the covalent bond between adsorbent and adsorbate is stronger than the original bonding in the adsorbent itself. Thus, when oxygen is adsorbed on charcoal and then is heated slightly to desorb, the resulting compound is not oxygen but CO or CO_2, indicating that the carbon-oxygen bond is stronger than the carbon-carbon bond of the charcoal.

As has been mentioned, in electrostatic attraction the force field falls off as the square of the distance between the objects, and in van der Waals attraction as the cube of the distance. The force field of covalent bonds falls off even more rapidly with distance, and as a result it is doubtful that covalent adsorbates lie more than one molecule thick on the active surface. The van der Waals forces, however, by their very nature polarized, are exerted over greater distances. Therefore, layers of several molecules thickness can be adsorbed in van der Waals adsorption.

Since adsorption occurs at the solid-liquid interface, it follows that, other things being equal, adsorbents with large surface areas per gram will adsorb large amounts, in grams adsorbate per gram of adsorbent. Therefore, although all surfaces show adsorption powers, the most effective adsorbents have the largest amount of surface area. Thus, the specific surface areas of commercial activated carbons are in the range of hundreds or even thousands of square meters per gram. For the same basic reason, particles of colloidal size are especially active as adsorbents.

As can be predicted from free energy and activity concepts the amount adsorbed per gram of adsorbent increases as the concentration of adsorbate in the liquid increases, up to the level at which the active surface is saturated, that is, completely covered. Thereafter further increases in concentration do not result in any increase in adsorption.

Solute compounds differ in their adsorbability. A number of conditions are of special interest in this regard. Large molecules are more strongly adsorbed than small ones. Polar groups such as -OH, $-NH_2$ decrease adsorption because they are attracted to the water and the adsorbent must overcome this attraction. For a similar reason, the more soluble compounds are the less well-adsorbed. The spatial arrangement of the groups in the molecule affects adsorbability; for example, branched chain acids are less adsorbed than straight chain ones. In the case of physical adsorption the difference in solute concentration between the bulk of the solution and the adsorbing surface is proportional to the change in the interfacial (surface) tension with concentration of adsorbate. Compounds that strongly decrease the surface tension of the liquid are adsorbed more strongly than those that do not. (Most substances decrease the interfacial tension of water.)

All of these considerations lead to the fact that in multicomponent systems adsorption is competitive among the various adsorbates. Even in a system which includes only water, a solute, and the adsorbent, there is competition between the adsorbate and the water, although water is only very weakly adsorbed on most adsorbents for organics. Therefore, the process of removing organics from waters, complex enough with single solutes, becomes even more complicated and intractable in practice.

Adsorbents, like collectors in froth flotation, are amazingly selective. For example, bone charcoal adsorbs the molecules imparting color to sugar liquors in the presence of a concentration of sugar molecules several hundred thousand times as great, even though sugar itself is a complex molecule presenting a variety of bonding opportunities including hydrogens, hydroxyls, carbonyls, etc.

Electrokinetics—

Electrokinetics refers to the motion of ions or molecules or particles along a gradient of electrical potential. Strictly, electrolysis involves the migration of ions, but since this is associated with a chemical change at the electrode, it is discussed later with the chemical mechanisms.

Particles, colloidal or suspended, in water usually bear a negative electrical charge. This electrical charge induces a positive charge in the immediately adjacent liquid layer. "Electrical double layer" is the term applied to this phenomenon. Thus, a difference in potential exists between the particle and the bulk of the solution beyond the region of influence of the induction, that is, across the electrical double layer. This difference, known as the electrokinetic potential, is also called the "zeta potential." For most colloids the electrokinetic potential is in the range of 30 to 60 millivolts.

Electrophoresis—refers to the movement of suspended charged particles that occurs when an electromotive force (i.e. a potential difference), is externally applied; the negatively charged particle is propelled toward the cathode, and the positively charged layer toward the anode. This constitutes a method for relocating organic particles in water. The velocity at which the movement occurs depends upon the gradient of the applied field. The rate standardized at a gradient of one volt per centimeter is called electrophoretic mobility. Most colloids have an electrophoretic mobility in the range of 2 to 4×10^{-4} cm/sec., which is only about one-half that of ordinary ions (except hydrogen and hydroxyl).

Electroosmosis—refers to the movement of water that occurs under an electromotive force when the particles are restrained from movement, as by a permeable membrane. This water movement is a method for relocating the organics. Much more important for the removal of organics than these macro movements (electrophoresis and electroosmosis) is the effect of electrical double layer in the micro movements involved in producing settleable particles from nonsettleable ones, as will be explained later under sedimentation.

Electrodialysis—is the final electrokinetic mechanism discussed here. An electrodialysis membrane is one which allows the selective electrokinetic passage of ions. In a cell made up of pairs of these membranes and subjected to electrodialysis, the anions in a compartment move through one membrane out of the compartment but the cations on the other side of this membrane cannot move into the compartment. The reverse is happening at the other membrane. As a result the solution in the compartment is depleted of ions. The primary use of electrodialysis in the water field is for removal of inorganic ions as in saline water conversion.

Freezing—

Freezing permits the separation of water from its impurities. When water containing a solute is frozen, the ice that precipitates contains none of the solute except that in microdroplets of a solution occluded as the ice forms. Thus freezing is a mechanism for producing pure water and a residual solution in which the solute is more concentrated than in the original. Considerable work has been done in this mechanism as a means of sea water conversion. The initial impetus was the fact that the heat required for freezing is only 1/7th of that required for distillation. However, when all factors are considered, the freezing process has only slight advantage thermodynamically over distillation for a process operating at a finite rate on sea water, containing 35,000 ppm of solute.

However, for wastewaters of approximately 1/100th this concentration, one of the disadvantages in sea water freezing, the lowering of the freezing point, practically disappears. Furthermore, the viscosity of pure water at its freezing point is about 30% lower than of sea water conversion brine at its boiling point and the thermal conductivity is higher. These factors might improve the washing and heat transfer as compared with the washing and heat transfer in saline water conversion.

To sum up, freezing is a mechanism for removing organics (and inorganics) but we are not sure how it will compare economically with distillation, a process which has already been ruled out on the basis of cost.

Hydration—

Hydration, like freezing, separates water from its impurities. Just as ice is a form of water in which the free energy is less than that of liquid water, so there are substances which will form ice-like solid compounds with water (hydrates) in which the free energy is also lower. Some of these are thermodynamically superior to ice because the phase change can be accomplished well above the freezing point of water. Hydrates typically contain 1 to 10 moles of water per mole of compound, but there are certain metallic salts and tetra alkylammonium salts that have 50 to 100 or more moles of water, and they are fairly insoluble in water. The impurities remain in the supernatant and the water is regenerated by warming the hydrate to its melting point. Low solubility and easy removal of the hydrating compound is a requirement.

Some gases that form hydrates have been studied as a means of saline water conversion. The lower hydrocarbons, methane and butane, form hydrates with up to 15 moles of water per mole of hydrocarbon (which brought them to the attention of the petroleum industry because they cause freeze-ups in pipelines). The water is regenerated by heating the hydrate to recover the hydrocarbon gas and water containing a small amount of hydrocarbon.

Such gas hydrates are clathrate (cagelike) compounds. The water molecules form a cage around the hydrocarbon molecule. The lattice structure of the resulting clathrate is different from that of ice. As an example of tactics based on theory, the large cage space in the lattice is about 70 nm in diameter. Therefore, molecules larger than this can be excluded as hydrate candidates.

Filtration—

Filtration is a seemingly simple but actually complex process for the separation of solids from water. It is one of the mechanisms for separation of organics that does not easily lend itself to categorization under a fundamental force. The mechanisms involved in filtration are many and they have been extensively studied and debated. The process itself may be described simply: under a hydrostatic pressure the filter medium will allow the hydrodynamic flow of water and dissolved matter but will restrict or prevent the concurrent transfer of particles and larger molecules. The filter medium may be a bed of sand or it may be a membrane including a simple screen. With a simple screen the separation process is clear and not subject to dispute. It is obvious that particles too big to pass through the openings in the screen will be retained while the water passes through both the screen and the body of retained particles.

The picture gets more complex as the size of the openings gets smaller. In such cases other forces come into play. Some filters will retain particles definitely known to be smaller than the pore sizes. The retention may involve electrostatic forces. It may be that the first layers of particles retained comprise a body in which the pores between particles are smaller than those in the medium so that the particles themselves become the filter medium and the medium itself merely their support. Or there may be a bridging effect whereby several particles arriving at a pore at the same time form a bridge which retains both the particles and subsequent arrivals even though the pore size of the medium could pass any of them individually. The goal of the design of such a filter is to retain the particles while maintaining a pore structure permeable enough to pass the water at economical rates.

Microfiltration or Ultrafiltration—

Microfiltration or ultrafiltration refers to a process which employs membranes with pores fine and uniform enough to retain specific size particles and pass smaller ones, and even to separate different sizes of molecules. The term microfiltration is sometimes applied erroneously to reverse osmosis, which also employs a membrane and a hydrostatic pressure, and provides for the retention of some components and the passage of others.

Microfilters are ordinarily the last step in removing organic particulates from water. From the previous description it can be seen that to obtain the maximum throughput of water, the feed water should have as few particles as possible, the bulk being removed by less expensive methods, and the particles shoud be as large as possible. Since the bulk of the organic pollutants in waters are in particulate form, e.g. municipal wastes, the removal of particulates is of primary concern. An additional consideration is the fact that the particulates and especially the colloids and their aggregates have the ability to adsorb dissolved organics and thus removal of these particulates results in removal of some of the dissolved organics.

Flocculation and Sedimentation—*

Flocculation and sedimentation subsume many of the fundamental mechanisms previously discussed. Though centrifuging is a form of sedimentation (and can generate forces hundreds and thousands times the force of gravity) our discussion here is directed to gravity sedimentation because the force and energy involved in this process are generally free of cost.

Table 4 shows the approximate rate of gravity fall of spheres of density 1.1 gm/cc in completely quiescent water. At these rates of fall, the slightest movement of the water or the slightest temperature differences resulting in a convection current would keep the colloidal particles in suspension forever. Also, it shows why it is desirable to agglomerate the particles into the largest size possible. Not shown is the fact that since the velocity is proportional to the difference in density between water and the particle, a particle of 1.2 gm/cc density instead of 1.1 gm/cc would fall at twice the velocity of the smaller. The 1.1 gm/cc density has been chosen as representative of an organic particle. Since the density of inorganic particles would be 2 gm/cc or even 3 gm/cc, it can be seen that the presence of inorganic particles incorporating or incorporated with the organics is very important for sedimentation rates.

The velocity is also inversely proportional to the viscosity of the water. Since viscosity is reduced steeply with temperature increases, even slight increases in temperature as from solar heating will increase the particles' settling velocity. However, such temperature increases also will generate convection currents which act to resuspend the particles. It is clear that the greatest effect on velocity is to be achieved by agglomerating the particles. In order to do this, it is necessary that the particles be brought into contact with each other. Three mechanisms accomplish this: Brownian motion, shear, and differential settling.

Brownian motion is the random displacement of small particles due to the random and unbalanced impacts on the particles of the water molecules in thermal motion. These random micromotions bring particles into contact with one another.

Shear occurs along the juncture of two volume elements of water moving relative to each other. Particles in or near the juncture are dragged past each other and contact occurs. Such shear forces may be natural, as with convection currents, or may be

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*(Note: There is ambiguity in the common use of the term flocculation. Some use flocculation to mean agglomeration, i.e. the coming together of particles to form larger aggregates. This no doubt comes about because the aggregates are called flocs. But the strict meaning of flocculation is as we here use it, namely the operation of slow stirring to induce agglomeration.)

Table 4. Approximate Rate of Fall in Water of Spheres, Density, 1.1 gm/cc

Diameter µm	cm/hr	cm/yr
100	200	—
10	2	—
1*	.02	200
0.1*	—	2
0.01*	—	2×10^2
0.001*	—	2×10^4

* = colloidal dimensions.

artificially induced by an operation called flocculation. In the latter, the liquid is stirred very gently by slowly moving paddles so as to allow contact opportunities without breaking up the delicate floc already formed.

Brownian motions are constant and cannot be controlled, but they do not interfere with settling because averaged over time, displacement is equal in all directions. Agglomeration by shear forces can be controlled, but such shear movements interfere with sedimentation and therefore flocculation is carried out separately from the sedimentation process.

Agglomeration through differential settling operates only in the sedimentation process itself. If the particles in a suspension are monodisperse, then each particle settles at the same rate and no particle can settle faster than another. Therefore, there are no contact opportunities and very little agglomeration will occur. However, if the system is polydisperse, the larger particles are settling faster than the smaller, and as a consequence, there are many collisions.

One force that keeps particles from agglomerating is their charge; because they carry the same charge, they repel each other and thus cannot come into contact and agglomerate. However, if a colloid bearing the opposite charge is added or if ions of opposite sign that can be adsorbed by the particle are added, the particle charge is neutralized and the particles can come into contact and agglomerate. That the mechanism is essentially electrostatic is shown by the fact that the required amount of oppositely charged ion to be added is reduced if that ion has a high valence.

Water has a high dielectric constant, that is, the strength of an electrostatic field is strongly attenuated with distance in water. Charged colloidal particles that are highly hydrated, that is, surrounded with a sheath of water molecules, tend to resist coagulation by added ions simply because the attraction between the ion and the particle is much reduced. Some highly hydrated colloids remain stable even though their electrokinetic potential is reduced to zero. The water sheath prevents contact. If a dehydrating agent, such as acetone or alcohol, is added, the sheath is destroyed and the colloid is again subject to coagulation by added ions.

Agglomeration does more than merely gather up the particulate material. By adsorption, the flocs can pick up dissolved molecules and carry them down in the sedimentation process. Flocs can be artificially formed by adding chemicals which themselves form colloidal, particularly gelatinous, masses which can be generated in substantial quantities. Flocs so formed are very effective in removing suspended colloidal and dissolved organics. Iron and aluminum salts are commonly used to form the the gelatinous hydrous oxide flocs which are insoluble in water and relatively easily settled.

The process of flocculation and sedimentation, involving as it does so many of the fundamental forces for relocation, is of primary importance in organics removal, and indeed by far the major portion of organics removal is accomplished by these processes. A first step in organics removal is to remove as much as possible through sedimentation, leaving the residual compounds in the supernatant for additional treatment.

CHEMICAL MECHANISMS FOR THE REMOVAL OF ORGANICS

Role of Free Energy

The free energy change determines whether an action can occur and in which direction it will proceed. It follows logically that the free energy change will also determine how far an action will go before it comes to a stop at an equilibrium condition. No reaction can occur unless the free energy of the products is less than the free energy of the reactants. And if the reverse reaction is possible, the larger the free energy change, the higher the ratio of concentration of products to concentration of reactants at equilibrium. If the reverse reaction is not possible the reaction goes to completion.

This does not mean that every reaction with a high free energy change can readily occur. With chemical reactions and with some physical processes, another energy condition must be satisfied. A reaction between two molecules is visualized as a coming together of the two, forming an ephemeral compound called the activated complex which then, as a result of rearrangement of atoms, breaks up into the reaction products. This will occur only if the collision of the two reactants has given the activated complex a certain minimum energy content. Otherwise, the two reactants simply fail to complete the reaction and will retain their individual charges. Even if the free energy content of the reactants is higher than that of the products, no reaction occurs unless there is additional energy available to raise the level of the reactants to the activated state. Thus, the rate of the reaction depends not simply on the rate of collisions between the reactants but upon the rate of collisions that have the necessary energy.

It is possible, by use of a discipline called statistical mechanics, which is not connected with thermodynamics, to calculate the frequency of collisions and also the frequency of collisions having an energy greater than that of the activated complex and thereby to explain and predict for a wide variety of reactions just how various forces, concentration, heat, light, catalysts affect the rate of reactions.

All the chemical reactions discussed in this section must follow those thermodynamic and kinetic laws. But we shall use them particularly in explaining the chemical mechanism of oxidation.

Chemical Oxidation

How far in the direction of complete destruction the oxidation reaction will go (or whether it will go at all) depends on the magnitude by which the free energy of the reactants exceeds that of the products. There is nothing that can be done about the free energy contribution of the organic materials, but that of the oxidizer reactant can be increased by changing the oxidant.

The free energy level can be measured as the voltage of a galvanic cell in which the reaction is or can theoretically be carried out. For an oxidant, it is expressed as an oxidation-reduction potential at a specified standard state. (Pressure, temperature, concentration). The higher the redox potential the higher the free energy contribution, and the more powerful the oxidant, i.e. oxidations that will not occur at all with oxygen as the oxidant can be carried out if a more powerful oxidant is used.

Since the end products, CO_2 and H_2O, have the same free energies regardless of how formed, this free energy contribution from a more powerful oxidant increases the free energy change upon reaction, but that does not affect the rate. But if the oxidant plus organic reactants have a higher free energy than the oxygen plus organic reactants, then the difference between the free energy of the reactants and that of the activated complex is reduced, and so a reaction can occur which cannot occur with oxygen.

The standard redox potential for dissolved oxygen is 1.23 volts. This measures the free energy that enzymes have to work with. With more powerful oxidants, chemical oxidations can be carried out even without enzymes or other catalysts. Chlorine, also an oxidizing agent, has a redox potential of 1.36 volts and accordingly can effect oxidations that even oxygen cannot bring about. (A small difference in voltage corresponds to a very large difference in free energy.)

Some other oxidants with high redox potentials are permanganate (1.52 and 1.67), ozone (2.07), and fluorine (2.85). The first two are now used for organic destruction in water. The last, fluorine, is the most powerful oxidizer known. A number of modern compounds should have high potential as oxidizers, including perchlorofluoride, $FClO_4$ nitrogen trifluoride, NF_3, alkali ferrates, Na_4FeO_4. One advantage of ozone is that, being composed solely of oxygen atoms, it leaves no deleterious residue in the water.

It is not necessary that the oxidation be complete in order to be useful. Incomplete oxidation can produce organic compounds more amenable to other removal or destruction methods. For example, the alcohol groupings, C-OH, can be oxidized to acid groupings, $C{=O \atop -OH}$. The hydrogen in an alcohol molecule grouping is not ionizable, but that of acid is, leaving an anion of the organic molecule which might be subject to removal by ion exchange.

Electrolytic Oxidation

Oxidizing reactions of interest in pollutant removal may occur at the anode where the migrating ions surrender electrons. The anion oxidized, i.e. neutralized, may not be the one that has migrated. The anion discharged, concentrations being comparable, will be that which has the lowest redox potential.

That often is the hydroxyl ion, OH^-:

$$4\,OH^- \rightarrow O_2 + 2H_2O + 4 \text{ electrons}$$

which has a redox potential of 0.4 volts. (The discharge generates oxygen, formerly called "nascent oxygen" from the concept that being new-born, it was especially active.) Modern experimentation and thermodynamic and kinetic theory, however, have shown that the electrode reactions generate very active groups called "free radicals," which are chemical groupings with very high energy content. In the hydroxyl case the free radical is $OH^{\cdot}$, a hydroxyl ion that has lost its electron but yet is not combined with anything else. These free radicals can react with each other, with other ions or compounds, or other free radicals near the electrode including our organic pollutant molecules. Or they can generate other free radicals, oxygen itself for instance, which having high energy content can react with organics that molecular oxygen itself cannot attack.

The problem is to get the proper ion to be discharged so that the productive free radicals are formed. Manipulation of this is possible through the phenomenon of overvoltage--the difference due to polarization and other effects, between the theoretical redox potential and the actual voltage at which discharge at a given current density occurs. The overvoltage varies with the nature of the anode material. On gold anodes the oxygen overvoltage can be as high as 0.9 volts, so one has a range up to 1.3 volts in which to maneuver.

Manipulation is also possible if the concentration of the competitive ion is adjusted. For instance, the redox potential of the hydroxyl ion, OH^-, the main competitor, is only 0.4 volts at the standard state, a concentration of approximately 1 mole per liter. While the concentration of pollutants is to be very low, in the parts per billion region, the concentration of the hydroxyl ion at pH6 is only about 2 parts per billion.

However, electrolytic oxidation as detailed above is not confined to the organic ions. The free radicals can oxidize equally well nonionized organic molecules in the near electrode region.

In some oxidation-reduction systems which are slow to reach equilibrium at the electrode, it has been found that the reaction rate may be increased by the addition of a very small quantity of a more active redox compound. The mechanism by which this is accomplished has yet to be explained. The material added is called a "potential mediator."

Electrolytic oxidation, a near-electrode process, should not be confused with chemical oxidation in which the oxidant is regenerated by electrolysis. That process, which takes place in the body of the liquid, is simply a chemical oxidation process, as already discussed. There have been a number of sewage electrolysis plants in the United States, wherein the chlorides in the sewage are converted to chlorine at the anode. The chlorine dispersed through the sewage acts as a chemical oxidizing agent (and disinfectant), producing chloride and the process is repeated. Peroxides can be similarly used.

Role of Radiation

Free radicals can also be generated in aqueous solutions by various kinds of electromagnetic radiation, and chemical reactions can be induced either by the action of the radiation directly, or by its effects on other chemical agents.

It is interesting to note that a reaction of the latter type, photosensitization, which as photosynthesis, is responsible for the production of carbohydrates, the most common organic compound produced. The formation of carbohydrates from CO_2 and H_2O involves a complex sequence of oxidation-reduction reactions, all enzyme catalysed. The main step is catalysis by chlorophyll. The chlorophyll absorbs the sunlight and transfers it to an unidentified organic compound which undergoes an oxidation-reduction reaction with water. Note, however, that the main reaction in this process is a reduction and an organic compound is synthesized rather than broken down.

Sunlight can also break down organic compounds (i.e. without an oxidant), by photolysis. Benzo(a)pyrene, for instance, has a half-life of less than a day in water exposed to sunlight. The half-life of para-cresol in similiar conditions is several hundred days. However, in the presence of humic acid this half-life is reduced more than ten fold, indicating that humic acids are photosensitizers for para-cresol.

Chemical Precipitation

Chemical precipitation is a common method for separating inorganic compounds from water. It has two forms. In one, a chemical is added that converts the compound into a less soluble one that precipitates and is separated. In the other, the added chemical does not produce a chemical change but merely reduces the solubility so that the compound precipitates. This is called salting out. Both forms are also possible for organic chemicals in general.

But while it is true that polluted waters containing organic particulate matter must also have some of this organic material in solution, the levels to which reduction is desired in toxic organics, pesticides, carcinogens, etc. are much below their solubility levels. Accordingly, there is little chance of precipitating them by merely reducing the solubility slightly. The only possibility is to change them into insoluble compounds by chemical reactions. Unfortunately, there is little chance of finding any chemicals that would produce insoluble compounds from the pollutants of importance, the solubilities of which are already in the μg/L and ng/L range. It is presented here as a theoretical possibility.

Ion Exchange

Ion exchange is a form of chemical precipitation that actually accomplishes what we have just stated to be unlikely. Although some would consider it a form of adsorption, ion exchange is a true chemical reaction in which the pollutant ion displaces an ion on the solid ion exchange medium. Chemical bonds are broken and formed, and the reaction can be written just as for any other chemical reaction, for example:

$$R - OH + P^- \rightleftharpoons R - P + OH^-,$$

and

$$R - H + P^+ \rightleftharpoons R - P + H^+$$

where:

R is the main portion of the ion exchange medium (R = resin)
$-OH$ is a hydroxyl attached by ionic bonding to the resin
P^- is a pollutant anion
$-H$ is a hydrogen attached by ionic bonding to the resin
P^+ is a pollutant cation
OH^- and H^+ are hydroxyl and hydrogen ions, or other anions or cations.

Note that the reaction is reversible. It therefore has an equilibrium position and is subject to all the thermodynamic laws governing equilibria. But this is a heterogeneous equilibrium, involving two phases, for the resin is a solid. By this reaction, the pollutant is fastened to the solid ion exchange resin, leaving the solution depleted in pollutant. Then, the solution removed, the R-P is regenerated to the hydroxyl or hydrogen form by contacting it with a small amount of alkali solution, acid or other ion and the attached pollutant moves into the liquid and is disposed of. One of the difficulties is that waters also contain inorganic anions and cations which will compete with the organic ions, and, since they are present in higher concentrations, will dominate that competition.

Ion exchange resins will also adsorb organic molecules, but this is a physical removal mechanism although the processing steps are identical with ion exchange: adsorption on the solid resin, removal of the water depleted of adsorbed material, and regeneration of resin to its original form.

BEYOND THE STATE-OF-THE-ART

The history of the interaction between science and technology has been that between the urge to know and the urge to do. For many centuries technology, the urge to do, was the prime mover in invention and the development of processes, much of which was done without an understanding of the fundamental theory. In the 18th century scientists began experimenting with and theorizing about natural phenomena without, in general, much thought about, or motivation by, their practical application. They or others took these fundamental discoveries and laws and used them in the invention and development of practical processes (and machines and techniques, but here we are concerned with processes). Thus science stimulated technology.

In the late 19th century something of a reversal occurred. The needs of technology and the zeal of inventors outdistanced the investigations of pure science and there was not only a great expansion in applying scientific discoveries to practical needs, but the technological needs began to stimulate new scientific investigation into fundamentals and theory. (There were, of course, technologists engaged in non-scientific based invention and pure scientists who followed where curiosity led.) Thus technology stimulated science.

When in the 1980s one reviews the subject matter and accomplishments of the numerous specialized scientific disciplines involved in removing organics from water, a surprising revelation emerges. To a large extent the work being done in each discipline as applied to organics removal is not being done by the outstanding specialists in that discipline. As a rough illustration, one can search the monographs on colloid chemistry by the acknowledged masters of colloid chemistry and find no mention of municipal wastewater. There is no mention in treatises on surface chemistry of the adsorption of water organics. Works on enzymology give little attention to enzyme catalysed oxidation of sewage organics. Solid state physicists are busy with transistors and are not intrigued by how loose electrons might be made to oxidize organics.

The bulk of the current work in applying fundamental principles to organics removal is being done by sanitary engineers, sanitary chemists, and others closely allied with the technology, who have been forced by that urge to grasp at competence in fields in which others are masters.

This does not mean to imply that creditable research is not done by such technologically oriented workers. Indeed, the best work in physical chemistry at present is being done by the chemical engineers. And certainly some understanding of the technological needs and possibilities is required to harness existing knowledge for the invention of superior removal processes or to create new knowledge to that end. For example, if one wanted to explore molecular orbital theory for possible removal of organic substances in water, one would not begin by contacting a sanitary engineer, as he would have to familiarize himself with molecular orbitals. Instead, a specialist in molecular orbitals should be contacted to undertake the fundamental research.

The original Office of Saline Water had the mission of finding ways to make potable water out of salt water, a task exactly corresponding to that of current interest, to free water from its organic impurities. A major undisputed accomplishment was its successful program of basic research into the properties and characteristics of water and its solutions. This was accomplished by seeking out the country's experts in the various disciplines and paying them to think about water. Money is a powerful stimulus to research.

It is not quite correct to say that this activity was undisputed. There are some who look down upon basic and theoretical research as an anomolous activity from which no forseeable and certainly no guaranteed result is forthcoming. Consider that just in the area of thermodynamics, there are certain individuals who believe unimaginable pipe dreams, such as frictionless pistons, quantities for which only the changes and not the actual amounts can be measured, processes that operate without any driving force and so slowly that nothing ever goes on at all, waves in a substance that does not exist, or barriers that have convenient tunnels through them. It is no wonder that in the non-scientific world and even to some extent in the engineering world, much that is termed theoretical or that whic [illegible] perimental in nature is dismissed as having no bearing on the real world. What would their reaction be if they knew that one of the world's greatest thermodynamicists, Joshia Willard Gibbs, never carried out an experiment in his entire adult career. He was a professor of mathematical physics, (as was Einstein). Yet students of physical chemistry can hardly avoid running into one or more of Gibbs' many deductions or equations, upon which whole industries are based.

A few decades ago the science of biology underwent a revolution. A group of biologists turned away from studying biology on a macro scale. They turned instead to biology on a micro scale -- how the cells worked, what the molecules were doing, how they responded to external challenge, how the atoms were put together in biological materials. They gave it a very descriptive name, molecular biology. The subsequent accomplishments of molecular biology are among the triumphs of science and technology in the second half of this century, now verging upon the actual chemical synthesis of life materials including the basic material of all life, DNA.

There is a distinguished professor who from his earliest days has had an unusual attitude toward the microorganisms he studies and uses. He considers them his friends, even his relatives. Anthropomorphic is the word for it. He calls them "bugs," and when he is thinking and talking about them he refers to an individual bug. He says: "the bug does this," or even more: "HE does this," and "HE doesn't like it there and wants to go here." In other words he has an intimacy with the bugs he studies. With regard to molecules, atoms, and electrons, this is the sort of intellectual intimacy that must be the habit of researchers who will next advance the technology of removing organics from water.

My assignment was to review the state-of-the-art as to fundamentals and not to project and certainly not to command the future. I find it necessary to say, however, that I believe that achievement in the future in the removal of organics from water and in water purification generally will come through directing the highest level of competence in a number of specialized fields, few of which have previously been concerned with water and wastewater, to an examination of the fundamental behavior of the molecules, atoms and forces involved in water cleansing. The following are some of the fields and disciplines that seem promising:

Thermodynamics of the molecules and reactions
Thermodynamic data on organics
Chemistry of surfaces, especially small size surfaces
Colloid chemistry
Solid state physics, of catalysts and of organics
The nature of chemical bonding
Enzyme catalysis and enzyme synthesis and tailoring
Electrokinetics, and electrophoresis
Exotic high energy oxidants

COAGULATION-SEDIMENTATION-FILTRATION PROCESSES FOR REMOVING ORGANIC SUBSTANCES FROM DRINKING WATER

James K. Edzwald

INTRODUCTION

"Among the principal failings of chlorination were odors and tastes produced by chlorine residuals, by plankton killed by chlorine, and by compounds formed with, or accentuated in odor or taste by, chlorine. Of special concern were the medicinal or iodoform-like tastes caused by traces ($\mu g/L$) of phenolic substances through the formation of chlorophenols." The above passage is from a paper[1] by Gordon M. Fair entitled "Fifty Years of Progress in Water Purification, 1913-1963." Formation of chlorinated organics from chlorinating water supplies containing certain organics was recognized as a problem in the early 1960's as indicated by Fair. In the past our analytical techniques were crude so that we measured the effects by tastes and odors, or we were able to screen water supplies for organic content only by using a gross, non-specific test--the carbon chloroform extract. In addition to tastes and odors our concerns regarding organics have intensified over the years. This is illustrated in Table 1. With the development of gas chromatographic techniques for measurement of specific organics in drinking water during the 1970's the problem of trihalomethanes was clearly identified.

Trihalomethanes (THMs) are produced within the water treatment system as byproducts of chlorination. A wide variety of organics, including dissolved, colloidal, and particulate forms, act as THM precursors. This chapter's goal is to describe the present state of knowledge regarding the removal of trihalomethane precursors from drinking water using the conventional treatment processes of coagulation, sedimentation, and filtration. Emphasis is placed on the removal of naturally occurring organic substances, the so-called humic substances, since they constitute the major fraction of THM precursors and their removal by the above processes is feasible. The removal of synthetic organic chemicals including pesticides derived from industrial sources or runoff is not considered here since these pollutants are removed more effectively by other processes such as adsorption, which is covered in another chapter.

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Table 1. Drinking Water Standards for Turbidity and Organics

Dates	Turbidity	Color	Organics	
1962-1976 (USPHS)	5 units	15 units	Alkyl benzene sulfonate	0.5 mg/L
			Carbon chloroform extract	220 μg/L
1977 (EPA)	1 unit	15 units*	Endrin	0.2 μg/L
			Lindane	4 μg/L
			Methoxychlor	100 μg/L
			Toxaphene	5 μg/L
			2,4-D	100 μg/L
			2,4,5-TP	10 μg/L
1979 (EPA)			Trihalomethanes (See below)	100 μg/L

Trihalomethane Regulations

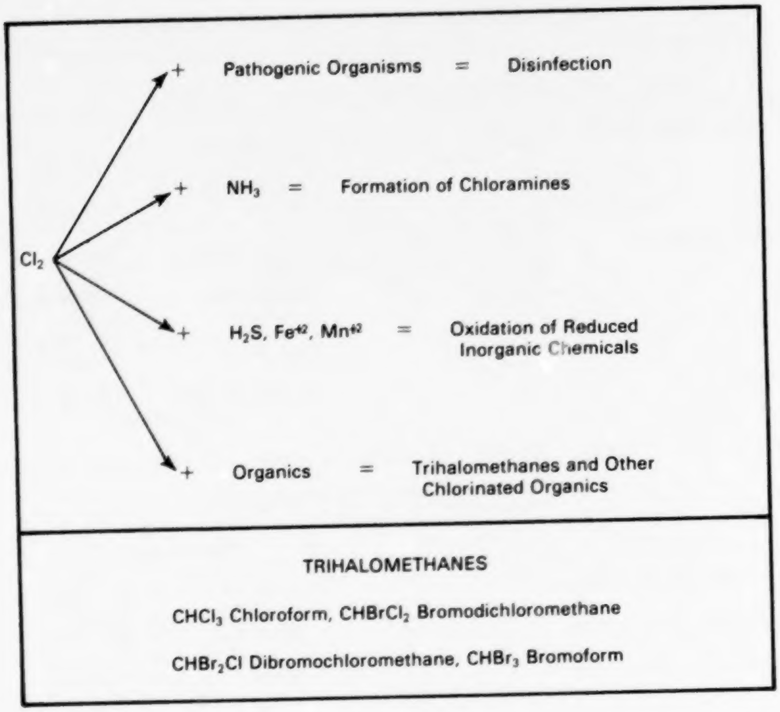
Systems	Effective dates	
75,000 persons or more	Monitoring:	Nov. 29, 1980
	MCL†:	Nov. 29, 1981
10,000-75,000 persons	Monitoring:	Nov. 29, 1982
	MCL:	Nov. 29, 1983
Less than 10,000 persons	Monitoring:	State discretion
	MCL:	State discretion

*Secondary standard
†Maximum contaminant level

This chapter has the following specific objectives: (1) to describe the formation of trihalomethanes; (2) to describe the principles pertaining to separation of particles by coagulation, sedimentation, and filtration; (3) to summarize our knowledge of concepts regarding organics removal by coagulation and filtration; (4) to illustrate the performance of actual water treatment plants in removing THM precursors and reducing THMs; and (5) to discuss possible water treatment process control parameters and THM surrogate measurements.

Background

When chlorine is added to water it can undergo various reactions depending on the constituents of the water. Fig. 1 illustrates some of the reactions which can occur and which can be viewed as parallel-competitive reactions. Disinfection is the primary reason for adding chlorine. The success of the water supply profession in the control of waterborne diseases has largely been due to the use of chlorine as a disinfectant in combination with other water treatment processes such as coagulation and filtration. Chlorination has been so successful and so widely used that its primary function is frequently forgotten. The first recorded use of chlorine in the United States as a disinfectant occurred in 1896 at the Louisville, Kentucky, Experiment Station[2]. Chlorination gained widespread acceptance in the United States after



Cl_2
+ Pathogenic Organisms = Disinfection
+ NH_3 = Formation of Chloramines
+ H_2S, Fe^{+2}, Mn^{+2} = Oxidation of Reduced Inorganic Chemicals
+ Organics = Trihalomethanes and Other Chlorinated Organics
TRIHALOMETHANES
$CHCl_3$ Chloroform, $CHBrCl_2$ Bromodichloromethane
$CHBr_2Cl$ Dibromochloromethane, $CHBr_3$ Bromoform

Figure 1. Possible parallel competitive reactions occurring when chlorine is added to water.

1908. As aptly stated in a report on "Drinking Water and Health" from the National Academy of Sciences[3], "The introduction of chlorination after 1908 provided a cheap, reproducible method of ensuring the bacteriological quality of water. Chlorination has come down to us today as one of the major factors ensuring safety of our drinking water."

In Fig. 1 we see that chlorine in the presence of ammonia results in the formation of chloramines (combined chlorine). Chloramines can also provide disinfection, although less efficient than free chlorine ($HOCl$ and OCl^-), and have been used in the United States for protection of distribution systems. Chlorine is also used to oxidize reduced inorganic materials (Fe^{+2}, Mn^{+2}, H_2S) whose presence is often troublesome. The last reaction is undesirable and was not recognized until the mid-1970's, although THMs have obviously been produced in water treatment plants as long as chlorination has been practiced. The detection of these compounds had to await the development and application of gas chromatographic techniques to drinking water. The major forms of the trihalomethanes are indicated at the bottom of Fig. 1.

The presence of THMs in drinking water was first reported by Rook[4]. In studies of the Berenplaat plant in the Netherlands, Rook showed that THMs were being produced during water treatment. He attributed the THM formation to the chlorination of waters containing humic substances which serve as THM precursors. About this time Bellar, et al.[5] reported that chloroform and other trihalogenated methanes were being produced as a result of the chlorination process during water treatment. In 1975 the U.S. Environmental Protection Agency (EPA) published the results of its study known as the National Organics Reconnaissance Survey (NORS)[6]. This 80-city survey showed the widespread occurrence of THMs in chlorinated drinking waters in the United States, and demonstrated that they result from chlorination. In general, total THM concentrations were related to the organic content of the water. It was also observed that higher concentrations of THMs were found when surface water was used as the water supply source, pre-chlorination was practiced, and more than 0.4 mg/L free residual chlorine was being used. The National Organics Monitoring Survey (NOMS) expanded upon the NORS study - 113 cities throughout the United States - and confirmed the occurrence of THMs in finished drinking water due to chlorination[7,8].

On February 9, 1978 EPA published[7] "proposed regulations" for the control of organic chemical contaminants in drinking water. These proposed regulations contained two parts. The first part set a Maximum Contaminant Level (MCL) of 100 μg/L for total trihalomethanes (TTHMs) in finished drinking water, and was proposed as being initially applicable to community water systems serving populations of greater than 75,000. The second part proposed granular activated carbon treatment for control of synthetic organic chemicals derived from industrial and agricultural sources, and urban runoff. After public hearings and comments, EPA issued a final rule[8] for control of THMs on November 29, 1979. EPA maintained the MCL of 100 μg/L for total trihalomethanes, but extended the coverage to include communities with populations less than 75,000 as indicated in Table 1. EPA also separated the granular activated carbon requirement from the THM regulations, and stated that regulations for the control of synthetic organic chemicals would be reproposed in the future.

Protection of the public health is a primary concern in setting drinking water regulations. Chloroform has been shown to be an animal carcinogen, and is suspected of being a human carcinogen[1,8]. Several factors were listed by EPA in setting a MCL for trihalomethanes. In summary they are [8]: "the potential human health risks of chloroform and other THMs; the fact that drinking water is the major source of human exposure to THMs; the fact that THMs are the most ubiquitous synthetic organic chemicals found in drinking water in the United States and are generally found at the highest concentrations of any such chemicals; the fact that THMs are introduced in the course of water treatment as by-products of the chlorination process and thus are readily controllable; that low cost and feasible means have been generally available since 1974 to reduce their concentrations in drinking water; that monitoring is feasible; and that the THMs are also indicative of the presence of a host of other halogenated and oxidized, potentially harmful by-products of the chlorination process that are concurrently formed in even larger quantities but which cannot be readily characterized chemically."

TRIHALOMETHANE FORMATION

Trihalomethane Measurements

THMs result from a series of complex reactions between chlorine and precursors. The precursors are largely humic macromolecules. Reaction pathways are generally unknown[9]. For the purpose of this discussion the THM formation reaction is examined through Equation (1).

$$\underset{\text{(Precursors)}}{\text{Organics}} + \text{Free Chlorine} + (\text{Br}^- \text{ or } \text{I}^-) = \text{THMs} + \text{Other Halogenated Organics} \qquad (1)$$

It is important to define three THM measurements[10]. All three measurements are useful; however, the selection of these measurements depends upon the intended use of the data.

Instantaneous THMs—

Instantaneous THMs (Inst THMs) is the concentration of THMs in a water sample at the time of sampling. At the time of sampling, any free chlorine present is quenched by adding a reducing chemical such as sodium thiosulfate or sodium sulfite. This halts the formation of THMs. The Inst THM measurement is applicable to the 100 μg/L TTHM MCL established for municipal water supply systems. Four samples are collected from the distribution system on a quarterly basis. One sample each quarter must be collected from the far end of the distribution system. Compliance is based on a running annual average of the quarterly samples. Fig. 2 illustrates Inst THM development in a treatment plant and in a distribution system. Note the higher Inst THM concentration in the distribution system compared to the treatment plant. Variables which affect THM formation in the distribution system - e.g., hydraulic residence time - are discussed in a subsequent section.

Terminal THMs—

Terminal THMs (Term THMs) is the concentration of THMs after storing an unquenched sample for a specified reaction period. As long as free chlorine is present the THM reaction will continue, and additional THMs will be formed. Depending on the precursor concentration this reaction may continue for periods of 7 to 10 days. The selection of the storage period depends on the intended use of the results. For example, if one is interested in the THMs which might be formed in the distribution system, then a storage period equivalent to the hydraulic residence time of the distribution system should be selected. Temperature affects the THM formation reaction, so storage of samples under controlled temperature conditions is important. One choice is to store the sample at a temperature similar to that of the water temperature in the distribution system. At the end of the storage period an aliquot of the sample should be used for measurement of free chlorine - the remainder of the sample is quenched and then used for THM analysis. An absence of free chlorine would indicate the THM reaction stopped, and therefore the THM concentration measured may not indicate the THM levels that could develop in the distribution system. The difference between the Term THM level in the treatment plant (e.g., water sample from the sedimentation tank) and the Term THM for water entering the distribution system as shown in Fig. 2 would indicate the reduction in THM precursors accomplished by treatment processes following sedimentation - e.g., filtration.

Trihalomethane Formation Potential—

Trihalomethane Formation Potential (THMFP) is the increase in the concentration of THMs which occurs during the storage period for determination of Term THMs - i.e., the difference between the Term THM concentration and the Inst THM concentration. It is a measure of the precursor level remaining in a sample at a point in the treatment plant or in the distribution system. For raw waters, prior to chlorination, one can determine its THMFP by chlorinating a sample in the laboratory with sufficient chlorine to maintain a free chlorine residual throughout the storage period. The sample is stored under controlled conditions of temperature and pH. THMFPs are illustrated in Fig. 2.

THM formation curves for raw water samples collected from the Grasse River are shown in Fig. 3. The Grasse River is a colored, low turbidity water supply in Northern New York and is typical of many surface supplies in that region as well as New England and other areas of the United States. The two curves illustrate differences in precursor levels for different times of the year. The lower THM formation curve is for water collected in February when the river was ice-covered while the other curve is for a sample collected in April during the spring runoff period. As illustrated the THMFP is time dependent and, of course, dependent on the precursor concentration. A higher THMFP resulted for the spring runoff sample which contained a nonvolatile total organic carbon (NVTOC) concentration of 6.3 mg/L.

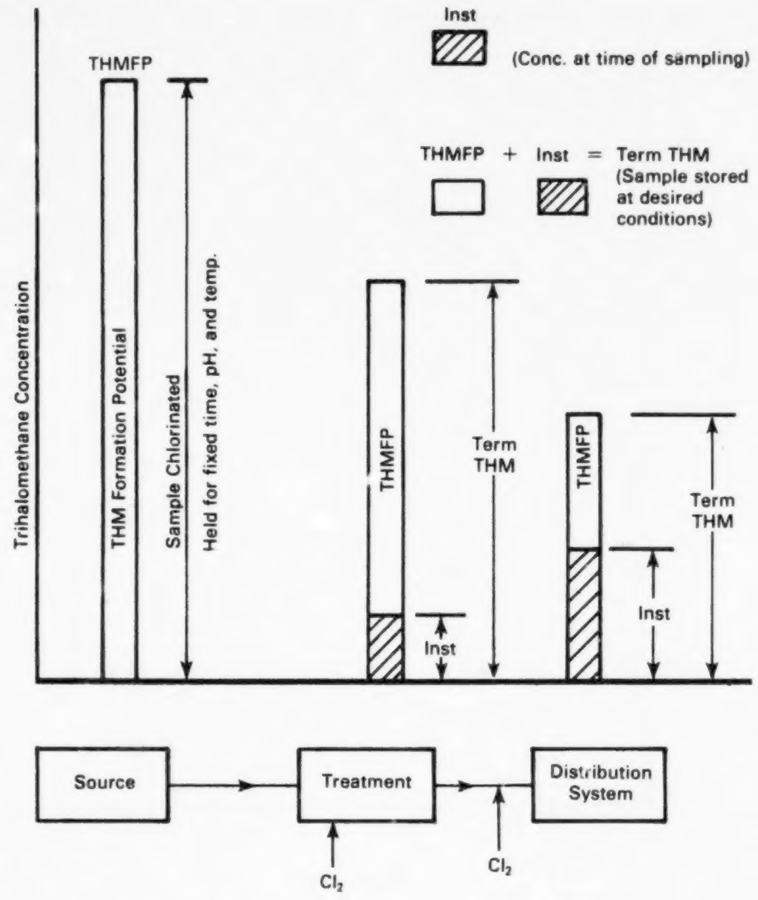

Inst
(Conc. at time of sampling)
THMFP + Inst = Term THM
(Sample stored at desired conditions)
Trihalomethane Concentration
THMFP
THM Formation Potential
Sample Chlorinated
Held for fixed time, pH, and temp.
THMFP
Term THM
Inst
THMFP
Term THM
Inst
Source
Treatment
Distribution System
Cl2
Cl2

Figure 2. Trihalomethane terminology.

Before discussing the factors which influence THM formation it is instructive to make an analogy with the widely used BOD (biochemical oxygen demand) test. The BOD test is used to measure the oxygen demand of water and wastewater samples due to the presence of biodegradable organics.

$$\text{Organics} + O_2 \xrightarrow[\text{bacteria}]{} CO_2 + H_2O + NH_3 \qquad (2)$$

We do not measure the organic matter (oxygen demanding precursors) directly, but rather we measure the oxygen consumed as a result of the biochemical oxidation of the organic matter by microorganisms. In essence the BOD test is a bioassay, which is time dependent and requires standard conditions. The test is influenced by a number of factors including: type of organic substrate, organic concentration, temperature, pH, and presence of trace elements. Dilution water, saturated with oxygen and containing trace elements and a phosphate buffer, is seeded with a bacterial culture. Standard conditions of a 5-day incubation period at 20°C are used.

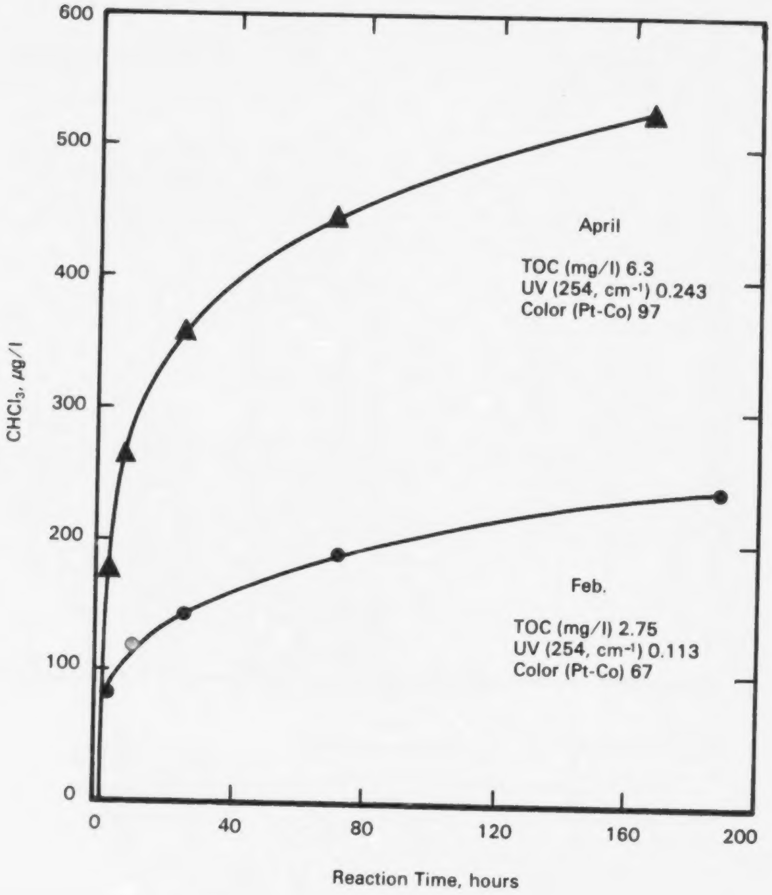


Figure 3. Chloroform formation curves for the Grasse River (Canton, NY). Samples collected in February and April; chlorination conditions: Cl_2 dose 15-20 mg/L, pH 7.5, 20°C.

The THMFP determination may also be thought of as a measure of organic contamination. It is an indirect measurement of THM precursors since we are measuring the effect of the precursor material. In order to determine the formation potential of a raw water sample, chlorine is added to the sample in the laboratory. While conditions covering storage (reaction) period, temperature, and pH have not been standardized, they influence THM formation and therefore in reporting results these conditions should be specified. The formation curves in Fig. 3 were developed at pH 7.5 and at 20°C with free chlorine available throughout the reaction period. The 7-day chloroform formation potentials ($CHCl_3FPs$) of the April and February samples were 532 μg/L and 237 μg/L, respectively. THM species other than $CHCl_3$ were insignificant. Note that the THM reaction for both samples was still proceeding after seven days.

THMFP measurements are useful for two reasons. First, they provide a measure of the precursor level in raw waters as previously discussed. Second, they provide a measure of the efficiency of treatment processes in removing THM precursors as shown schematically in Fig. 2. This is particularly useful in pilot plant studies or treatment plant evaluation.

Factors Affecting THM Formation

Factors influencing THM formation have been discussed in several publications[10–14]. These factors include nature and concentration of precursors, pH, temperature, chlorine dose, and concentration of bromide ion. The reader is referred to the publications for detailed discussion of these factors; here, some summary comments are presented.

A wide variety of organic substrates can act as THM precursors. Humic substances are considered a major source of precursor material. However, "humic substances" is a broad classification as will be noted in a subsequent discussion. Morris and Baum[9] have presented data showing that naturally occurring soluble organics other than humics are also THM precursors. These organics included pyrrolic-type compounds (found in chlorophyll) and acetogenins (natural pigments). Rook[15] has investigated the chlorination of natural glycosides including hesperidin, heperetin, rutin, and phlorizin. He used these compounds because they contain hydroxylated aromatic rings with two free meta-positioned OH-groups which he proposes as the active sites for trihalomethane formation. Of interest to water utilities obtaining their drinking water from reservoirs is that algal cells and algal cell by-products are also THM precursors[16–18].

A convenient way to examine THM formation data is by expressing it in terms of $CHCl_3$ yields defined here as μg $CHCl_3$ produced per mg total organic carbon (TOC) for extended chlorine reaction periods. The data in Table 2 are limited, but do show $CHCl_3$ yields for humic acid, algal biomass and extracellular products, and two natural waters. It is interesting to note that the $CHCl_3$ yields for the Grasse River are approximately equal even though the THM precursor level in the river during spring runoff (April sample) was higher than that in the winter (February sample), as previously shown in Fig. 3. There can be a large variation in yields due to differences in the nature of the THM precursors, pH conditions, temperature, and chlorine contact period.

Seasonal variation in temperature will influence THM formation. In general, greater THM formation occurs with increasing temperature. Stevens and Symons[10] have reported that approximately twice as much $CHCl_3$ was produced from Ohio River water at 25°C as at 3°C. Using these data Kavanaugh et al.[14] have determined third-order kinetic rate constants for THM formation in which the rate constant doubles for every 10 degree increase in temperature between 0° and 30°C.

In general, an increase in THM formation is found at higher pH. This is due to the final hydrolysis reaction which requires alkaline conditions. Morris and Baum[9] have presented data which show that THM formation can continue after the free chlorine has been quenched if the pH is raised. This suggests that if chlorination is practiced at pH 6 to 7, additional THM formation can occur when the pH of the water is raised even if no free residual chlorine is present. This indicates the presence of chlorinated intermediates. The effect of pH on the $CHCl_3$ yield of humic acid is shown in Table 2. The data of Stevens et al.[11] show twice the yield at pH 9.2 as at pH 6.7. Clearly, pH is an important parameter in evaluating THM data for distribution systems, treatment plants, and pilot plants and should be measured and reported.

Bromide and iodide ions are oxidized by aqueous chlorine to species capable of organic substitution reactions resulting in formation of brominated (or iodinated forms) forms of the trihalomethanes[20]. For fresh waters, chloroform is the dominant THM produced. In the presence of Br^- which can occur in water supplies subject to salt water intrusion, there is a shift to the brominated forms[12,13,21].

Table 2. TOC and Chloroform Yield Data

Water	TOC mg/L	pH	Cl_2Contact Period hrs	Yield µg $CHCl_3$/mg/TOC	Comments
Humic acid	2.31	8.1	135	128	Humic acid extracted from Mich. peat (Edzwald[19])
Humic acid	3.85	8.1	135	128	
Humic acid	~0.6	6.7	96	70	Commercial humic acid (Stevens et al.[11])
Humic acid	~0.6	9.2	96	140	
Grasse River	2.75	7.5	191	87.3	See Figure 3
Grasse River	6.3	7.5	168	84.4	
Stonelick Lake	7.27	8.0	141	83.0	Northeast of Cinc., Ohio (Edzwald[19])
Algal biomass	2.1-75.8	7.5,9.3	Not specified	19.9-398.4	Four algal species (Hoehn et al.[17])
Algal extracellular products	-	7.5,9.3	Not specified	3.98-498	

COAGULATION, SEDIMENTATION, AND FILTRATION IN WATER TREATMENT PRACTICE: PRINCIPLES

Introduction

The coagulation process involves both the chemical destabilization of particulates and the physical transport of destabilized particles resulting in particle collisions to form larger aggregates called floc. The latter step - particle transport - is the rate limiting one, and is referred to as flocculation.

Particulates in water supplies are normally removed through a series of processes consisting of coagulation-flocculation, sedimentation, and filtration. This is illustrated in Fig. 4 for a conventional water treatment plant. An objective is to remove most solids by sedimentation leaving the filtration step as a polishing process. In the conventional water plant one is interested in using chemical coagulants in such a way that raw water particulates are flocculated into aggregates large enough for settling.

Particulates can also be separated without sedimentation in which all of the solids are removed in the filters - direct filtration. A schematic of direct filtration is shown in Fig. 5. Direct filtration may include a flocculation tank or one can bypass this process and go directly to the filters (in-line filtration). In either case it is necessary to add chemical coagulants before filtration to destabilize the particles in the raw water. A listing of each process used in conventional treatment and direct filtration plants is presented in Table 3 with appropriate design and operating criteria.

In this section general principles regarding the nature of particles in water supplies and water treatment practice are presented. These depict the state of our knowledge and emphasize developments in the last 10 to 20 years.

Particles

The type, size, and concentration of particles affect their behavior in water treatment systems. Raw water supplies may contain inorganic particulates such as asbestos fibers, clays, and silts. Within the treatment plant, coagulant precipitates (e.g., $Al(OH)_3(s)$) may be produced, adding to the particle mass and concentration. Raw waters may also contain organic particulates such as humic substances, viruses, bacteria, and plankton. These particles cover a broad range of sizes from the nanometer end for humic substances and viruses to tens of micrometers for plankton and coagulant precipitates. It is significant that the bulk of these particles are classified as colloids. Although colloids are generally considered as ranging in size from 1 nm to 1 μm, no exact boundaries exist. Colloidal systems may contain small particles and large molecules (e.g., humic substances). Colloidal particles are distinguished by their large surface areas per unit volume and by their light scattering properties. Colloidal systems scatter light (Tyndall effect) whereas true solutions scatter very little light. Turbidity, which is used in controlling the operation of water treatment plants, involves measuring the light scattering properties of a water sample.

A few considerations regarding turbidity measurements follow. The amount of light scattered (turbidity) depends on the number, size, shape, and refractive index of the particles as well as the wavelength of the incident light, and the geometry and detection characteristics of the turbidimeter. In water treatment, turbidimeters have been standardized only to the extent that the light scattered at an angle of 90° to an incandescent lamp source is measured. Even this is a recent development as prior to the mid-1970's a variety of instruments measuring scattered and transmitted light were used, including the Jackson Candle Turbidimeter.

It is important to emphasize a few points about the information turbidity measurements do or do not provide. Much of the material presented here was taken from *Drinking Water and Health*[3], O'Melia[25], and Friedlander[26]. Turbidity measurements are extremely useful as an indication of water quality and as an operating control

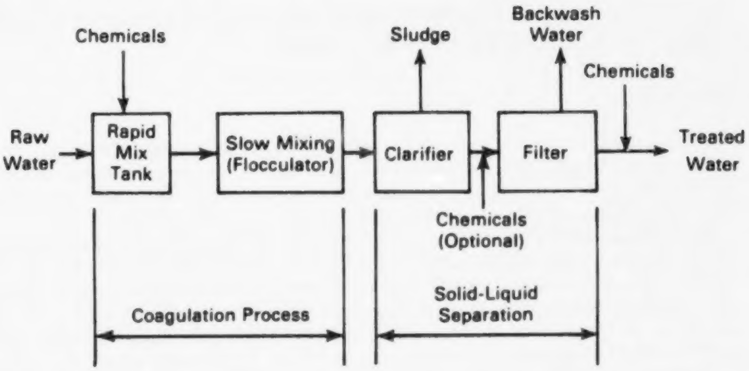

Chemicals
Sludge
Backwash Water
Chemicals
Raw Water
Rapid Mix Tank
Slow Mixing (Flocculator)
Clarifier
Filter
Treated Water
Chemicals (Optional)
Coagulation Process
Solid-Liquid Separation

Figure 4. Conventional water treatment plant.

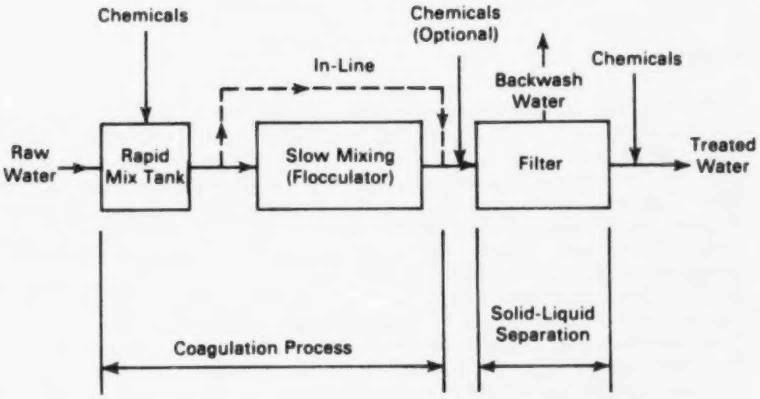

Chemicals
Chemicals (Optional)
In-Line
Chemicals
Backwash Water
Raw Water
Rapid Mix Tank
Slow Mixing (Flocculator)
Filter
Treated Water
Coagulation Process
Solid-Liquid Separation

Figure 5. Direct filtration.

parameter in water treatment plants. The measurements can be made easily and rapidly, and the instrumentation is relatively inexpensive. Turbidity measurements do not give complete information on the size, number, mass, or type of particles. Small particles (e.g., maximum dimension less than about 0.1 μm) do not scatter much visible light. Therefore a water containing asbestos fibers, viruses, or humic substances may have a large particle number concentration, but a low turbidity. Larger particles such as clays or plankton which have particle diameters approximately the length of visible light scatter light more effectively and thus would yield higher turbidities. This is illustrated by the examples below and use of Figs. 6 and 7.

Table 3. Design and Operating Parameters: Conventional Treatment and Direct Filtration (From Refs. 22-24)

Process/Parameters	Conventional	Direct Filtration
Rapid mix tank		
Detention time, sec	30-300	Optional*
Velocity gradient, sec $^{-1}$	700-1000	(pilot plant studies)
Flocculation tank		
Detention time, min	30-60	Optional*
Velocity gradient, sec $^{-1}$	10-100	(pilot plant studies)
$G\bar{T}$	10^4-10^5	
Sedimentation tank		
Detention time, hr	4	Not applicable
Overflow rate, m^3/m^2-day	37-49	
Filtration		
Sand filters		Not applicable
Filtration rate, m/hr	4.9	
Effective size, mm	0.45-0.55	
Media depth, m	0.6-0.76	
Dual media filters		
Filtration rate, m/hr	4.9-19.5	4.9-19.5
Effective size, mm		
Anthracite	0.9-1.2	0.9-1.2
Sand	0.45-0.55	0.45-0.55
Media depth		
Anthracite, m	0.46-0.61	0.38-0.90
Sand, m	0.38-0.46	0.20-0.30

*Mixing including flocculation: detention times of less than 1 min. to 40 min.

Case 1: Raw water containing 5 mg/L humic material
Assume: particle density (ρ) of 1.01 g/cm^3 and particle diameter of 0.021 μm.
Particle number: 10^{12} particles/cm^3

This water would scatter very little light so that its turbidity would be approximately 1 NTU as shown in Fig. 7.

Case 2: Raw water containing 5 mg/L clay
Assume: ρ of 2.5 g/cm^3 and particle diameter of 1.6 μm.
Particle number: 10^6 particles/cm^3

This water would contain a particle number concentration six orders of magnitude less than that of Case 1, but its turbidity would be higher than Case 1 - e.g., 5 mg/L kaolin clay would have turbidity of 7 to 8 NTU.

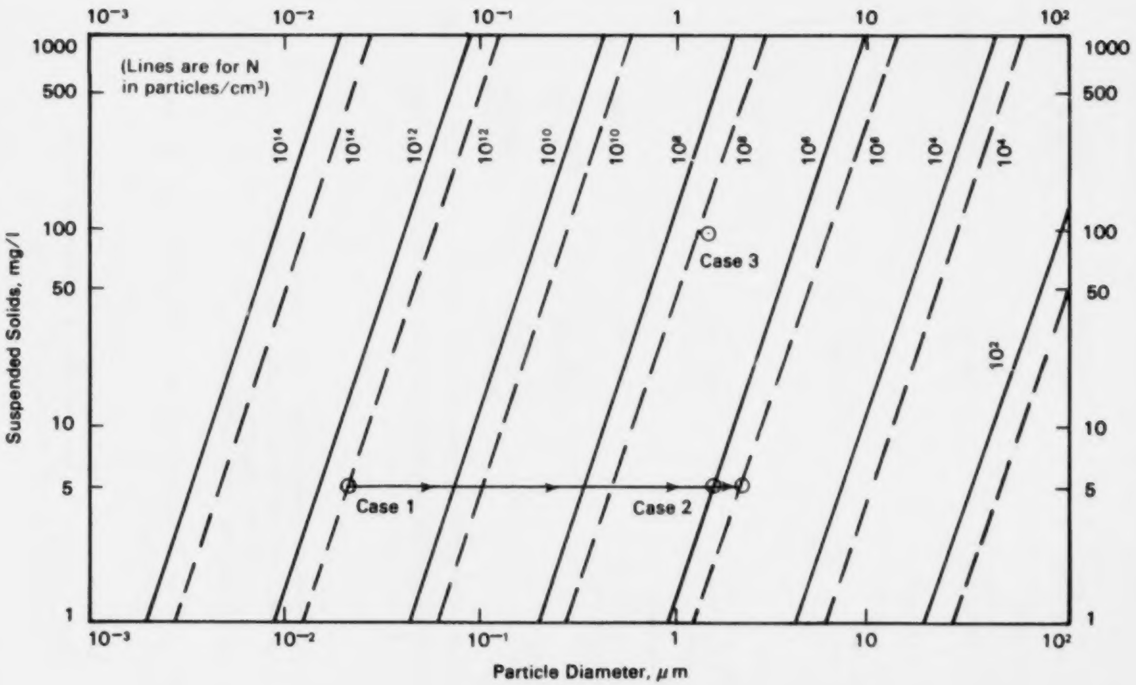


Figure 6. Isoparticle number concentrations (N) in particles per cm³ (Solid lines, particle density 2.5 g/cm³, dashed lines, particle density 1.01 g/cm³. Cases refer to examples in text.).

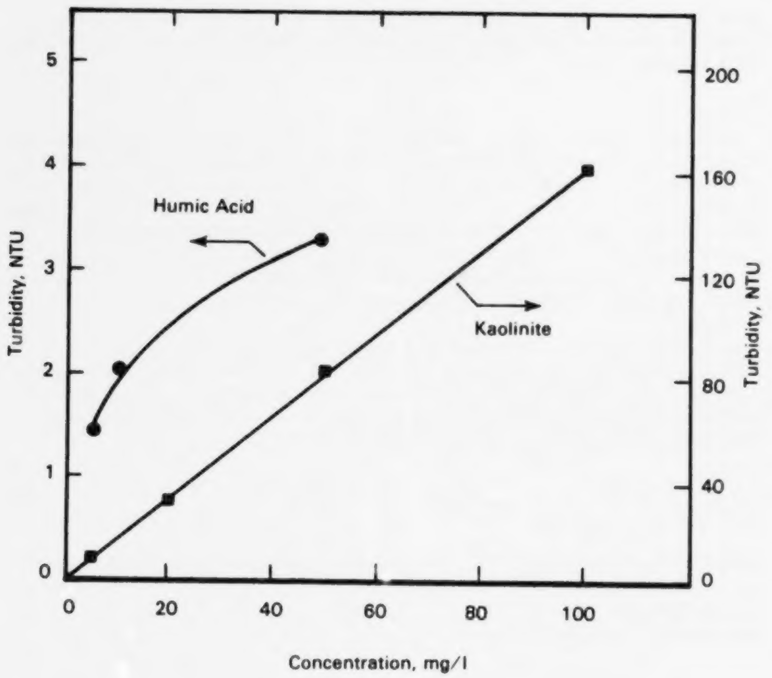


Figure 7. Turbidity vs. solids concentration for humic acid and kaolinite.

Coagulation-Flocculation

As mentioned earlier coagulation in water treatment involves two separate and distinct steps. First, stable particles are rendered unstable or "sticky" by the addition of chemicals (coagulants). Second, collisions among particles are induced resulting in the formation of particle aggregates or floc. A schematic flow diagram of the coagulation process in a conventional water treatment plant is shown in Fig. 4. The first step is fast, occurs in the rapid mix tank, and although a simplification, is referred to as a chemical step. The second step involves physical transport of particles and is the rate limiting step. This step is carried out in flocculation tanks with gentle mixing for periods of 30 to 60 minutes.

Particle Destabilization—

Theories of colloid stability are described in a number of references[27-29]. Applications to the water treatment field were made by a number of investigators including: A.P. Black, C.R. O'Melia, J.J. Morgan, W. Stumm, and their students Particle destabilization may be accomplished by four mechanisms: (1) compression of the electrical double layer by addition of electrolyte, (2) adsorption/charge neutralization, (3) interparticle bridging, and (4) enmeshment of colloids in a precipitate of a metal hydroxide. Compression of the electrical double layer occurs naturally in saline waters (estuaries and oceans)[30] but the salt concentration required for effective destabilization is too high for water treatment applications. Aluminum (III) and iron (III) salts can accomplish particle destabilization by both charge neutralization and enmeshment of colloids in a precipitate ("sweep floc"). Polyelectrolytes, depending on their charge and molecular weight, can accomplish destabilization by charge neutralization or by interparticle bridging. Specific coagulants are discussed later in greater detail.

Particle Transport—

Collisions between particles can occur by: (1) Brownian diffusion (perikinetic flocculation), (2) bulk fluid motion (orthokinetic flocculation), and (3) differential settling in which a particle that is settling rapidly overtakes and collides with a particle settling at a slower rate. The aggregation of particles depends upon the rate of collisions between particles (particle transport), and whether the particles "stick" together (particle destabilization) upon colliding. Theories of particle transport for coagulation were presented by Smoluchowski[31] in 1917. Application of Smoluchowski's theories to design of flocculation basins was presented by Camp[32,33] and later by Hudson[34,35].

It is instructive to present some simple equations for flocculation and discuss the influence of particle size on particle collisions. The concepts have been developed by O'Melia[28,29] and Friedlander[26]. For a suspension of particles of uniform size (monodispersed or homogeneous), the rate of change in the total concentration of particles for perikinetic flocculation (Brownian diffusion) is:

$$\frac{dN}{dt} = -\frac{4}{3}\frac{kTN^2}{\mu} \qquad (3)$$

in which N is the total number concentration of particles at time t, k is Boltzmann's constant, T is the absolute temperature, and μ is the fluid viscosity. For a homogeneous suspension subjected to agitation causing velocity gradients (orthokinetic flocculation), the equation is:

$$\frac{dN}{dt} = -\frac{2}{3} G\, d^3\, N^2 \qquad (4)$$

in which G is a mean velocity gradient (time^{-1}) and d is the diameter of the particles.

Both equations assume destabilization is complete; that is, the particles are sticky so that each collision is successful. For monodispersed suspensions flocculation due to differential settling cannot take place. The ratio of the rate of orthokinetic flocculation to perikinetic flocculation is:

$$\frac{\text{Ortho. Rate}}{\text{Peri. Rate}} = \frac{1/2\, G\, d^3\, \mu}{kT} \qquad (5)$$

For water at 25°C, 1-μm diameter particles, and a velocity gradient of 10 sec^{-1} this ratio is unity. In other words particle transport by Brownian diffusion equals that caused by gentle stirring. It can also be shown that particle transport efficiency is at a minimum for 1-μm diameter particles. For particle diameters less than 1μm, Brownian diffusion becomes predominant and orthokinetic flocculation becomes negligible even for high values of G. For particles greater than 1μm, particle transport by stirring becomes predominant.

Equations for heterogeneous suspensions are cumbersome. O'Melia[25] has discussed the effect of particle sizes on flocculation kinetics for collisions between particles of two different sizes. The following conditions were considered: temperature of 20°C, particle specific gravity of 1.02, and velocity gradient of 10 sec^{-1}. Collision rates were calculated for particles with diameter of 10μm undergoing collisions with particles varying in diameter from 0.01 μm to 1000 μm. For this heterogeneous system a minimum in contact efficiency is observed, but the minimum efficiency occurs for a broad particle size range - approximately, 0.1μm to 1 μm.

Brownian diffusion is predominant only for particle diameters less than 0.01 μm. Collisions by shear (stirring) predominate over a wide range - particle diameters of 0.01 μm to 100 μm. Differential settling becomes significant as particle diameter approaches 100 μm. O'Melia[25] has pointed out that flocculation tanks can be effective if the suspension is heterogeneous and contains larger particles. In water treatment practice, operators produce heterogeneous suspensions by adding particles such as clays or by practicing "sweep floc" coagulation.

Chemical Coagulants—

Salts of aluminum (Al(III)) and iron (Fe(III)) are widely used as coagulants. How they function as coagulants requires an understanding of the chemistry of the hydrolysis of these metal ions. Alum is used here as an example, although iron behaves in an analogous fashion. Much of our knowledge regarding the chemistry of alum with respect to coagulation was developed in the 1960's. Alum ($Al_2(SO_4)_3 \cdot 14H_2O$) dissolves readily in water releasing SO_4 ions to solution. The Al^{3+} (actually a shorthand since it exists as $Al(H_2O)_6^{3+}$) undergoes hydrolysis reactions, some of which follow:

$$Al^{3+} + H_2O = AlOH^{2+} + H^+ \tag{6}$$

$$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+ \tag{7}$$

$$Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+ \tag{8}$$

$$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+ \tag{9}$$

$$8Al^{3+} + 20H_2O = Al_8(OH)_{20}^{4+} + 20H^+ \tag{10}$$

Protons are liberated making alum an acid. The aluminum species formed depend on the pH of the water and the alum dosage. Fig. 8 shows the solubility of $Al(OH)_3(s)$ in water with the distribution of major dissolved species as a function of pH.

Due to its chemistry, alum can act as a coagulant in two ways. In many applications, sufficient alum is added so that $Al(OH)_3(s)$ is precipitated. The shaded area in Fig. 8 illustrates conditions of pH and alum dosage where this is favored. Colloids in the raw water become enmeshed in the $Al(OH)_3(s)$ precipitate. The gelatinous precipitate that is formed is sticky enough that aggregation of floc is achieved. The precipitation of aluminum hydroxide generates additional particles which improves the kinetics of particle aggregation. This is important in the coagulation of low turbidity waters, since additional particles are needed for particle aggregation given the flocculation period typically found in water treatment plants. This method of coagulation is often termed "sweep floc."

Alum can also accomplish coagulation by the adsorption of positively charged monomers (e.g., $AlOH^{+2}$) and polymers (e.g., $Al_8(OH)_{20}^{4+}$) on negatively charged colloids. This adsorption is strong and can result in particle destabilization by charge neutralization. The availability of these positively charged aluminum species depends on pH and the alum dosage. Turning our attention to flocculation kinetics, particle destabilization by charge neutralization would have application in treating raw waters containing high concentrations of particles. For low turbidity waters, particle destabilization can also be achieved; however, floc formation would be limited due to insufficient numbers of particles to produce a high rate of collisions among particles. It is noted that polymeric forms of aluminum exist as intermediates in the precipitation process, and that they play a role in coagulation even when "sweep floc" is practiced, particularly at slightly acid pH conditions.

The use of synthetic organic polymers to improve solids-liquid separation has been one of the most significant developments in water treatment technology in the last 25 years. Increasing use of polymers in water treatment has taken place during

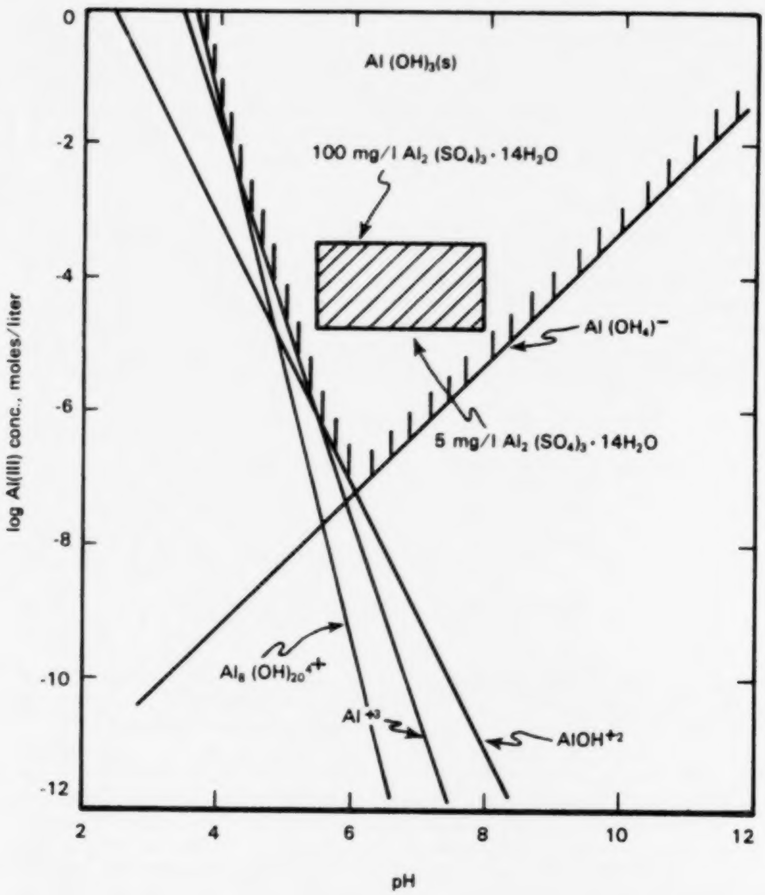
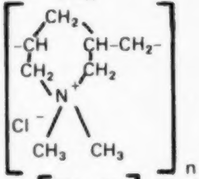
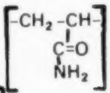
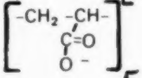
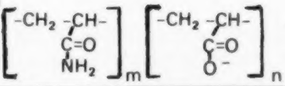


Figure 8. Solubility of Al(OH)$_3$(s) in water (Shaded area is the concentration-pH range often used for alum in water treatment).

the last 10 years. Many commercial polymers have been approved by EPA for use in potable water treatment[16].

A polymer is a chemical structure characterized by a series of repeating chemical units (monomer units) held together by covalent bonds. A summary of polymer examples is listed in Table 4. Cationic (positive charged) polymers are used as primary coagulants and coagulant aids. They are also used as filter aids and in sludge dewatering as chemical conditioners. Most cationic polymers being produced for treatment applications have molecular weights less than 10^5. These polymers tend to accomplish particle destabilization by adsorbing on negatively charged colloids thus producing charge neutralization at the proper dosage. At low turbidities particle destabilization can be achieved, but the kinetics of flocculation would be slow due to poor particle contact opportunities.

Table 4. Examples of Polymers

Charge	Structural Type/Functional Group	Molecular Weight
Cationic	Polyethylenimine $[-CH_2-CH_2-N^+H_2-]_n$	600 to 50,000-100,000
	Polydiallyldimethyl-ammonium chloride ("Cat-Floc") 	Variety of Cat-Floc types available, M.W. 10^4 to 10^5
Nonionic	Polyacrylamide  $\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]$	$\sim 10^6$
Anionic	Polyacrylic acid  $\left[-CH_2-\underset{\underset{O^-}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]$	$\sim 10^6$
	Hydrolyzed polyacrylamide  $\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]_m\left[-CH_2-\underset{\underset{O^-}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]_n$	$\sim 10^6$

Nonionic (no charge) and anionic (negative charged) polymers are produced with molecular weights usually in excess of 10^6. These polymers are used as coagulant aids, filter aids, and in sludge conditioning. These polymers function by forming particle-polymer-particle bridges - i.e., interparticle bridging. Size of the polymer is important. Molecular weights of 10^6 or more are necessary for the polymers to bridge colloidal particles to form floc. Earlier comments regarding the influence of particle numbers (turbidity) on flocculation kinetics are applicable.

Filtration

As shown in Figs. 4 and 5 filtration is used in conventional water treatment plants and direct filtration plants for the purpose of solids removal. The subject of filtration is extensive, and the body of knowledge represents an accumulation over the last 90 years. Thus no attempt is made to review this subject here. An excellent review of deep bed filtration with applications to water treatment can be found in a publication of Baumann[37]. What is stressed here is the importance of particle destabilization (pretreatment) for filtration and some analogous features of filtration coagulation[38-40]

Filtration is a two step process: particle transport and particle attachment. Particle transport involves the transport of destabilized (sticky) particles from water to the surface of the collector. A single spherical grain of filter media - single collector - is considered in which under laminar flow conditions particles may be transported from the flowing fluid to the collector by three mechanisms: Brownian diffusion, interception, and sedimentation. The removal efficiency (η) of this single collector is defined as follows:

$$\eta = \frac{\text{Rate at which particles strike collector}}{\text{Rate at which particles approach collector}} \qquad (11)$$

Equations for η for each transport mechanism follow:

$$\eta_D = 0.9\left(\frac{kT}{\mu\, d_p\, d_c\, v_o}\right)^{2/3} \tag{12}$$

$$\eta_I = \frac{3}{2}\left(\frac{d_p}{d_c}\right)^2 \tag{13}$$

$$\eta_S = \frac{(\rho_p - \rho)\, g\, d_p^2}{18\, \mu\, v_o} \tag{14}$$

$$\eta_{Total} = \eta_D + \eta_I + \eta_S \tag{15}$$

Here D, I, and S stand for diffusion, interception, and sedimentation, respectively. In addition, k is Boltzmann's constant, T is the absolute temperature, μ is the fluid viscosity, d_p is the diameter of the particles being applied to the filter bed, d_c is the collector diameter (filter media), v_o is the filtration rate, ρ_p and ρ are the densities of the suspended particles and water, respectively, and g is the gravitational constant.

It is noted that coagulation and filtration are analogous in that both are two step processes involving particle transport and particle sticking (destabilization). As in coagulation, there is also a suspended particle size, or size range, in which there is a minimum in particle transport efficiency. Equations (12) - (15) are used to illustrate this for the following conditions: temperature of 25°C, particle density of 1.01 g/cm^3, collector diameter of 0.5 mm, and filtration rate of 2 gpm/ft^2 (4.9 m/hr). The results are plotted in Fig. 9. As in coagulation, small particles (say 1 μm or less) are removed by transport from the water to the filter media by Brownian diffusion. Particles greater than about 5 μm are transported effectively by settling and interception. There is a size range, in this case about 1 μm to 5 μm, in which there is a minimum in transport efficiency. Note that particle straining has not been discussed. Many believe straining is the main way in which filters function. Particle straining is not a dominant mechanism in deep bed filtration unless the particles being applied to the filter are quite large. It would also be characterized by very shallow penetration into the filter and rapid clogging requiring frequent backwashing. Straining occurs when the suspended particle size is greater than $0.2 d_c$ (0.2 times the collector diameter). Thus for 0.5-mm filter media, straining would be important for suspended particles greater than 100 μm. The bulk of the particles being applied to filters in water treatment are smaller than 100 μm.

Recent work in filtration has demonstrated the role of retained particles or "dirty" bed filtration[40,41]. Suspended particles are initially removed by the clean bed; however, these retained particles then act as additional collectors so that one gets particles "sticking" to previously retained particles as well as the original filter media. This increase in collectors improves filtration and provides an explanation for the observed phenomenon of filter bed ripening in which filtration performance improves with time immediately after backwashing. Sticking of particles to surfaces including particle-particle sticking can be quite strong when polymers have been used for particle destabilization. Particles sticking to presumably clean surfaces and to each other occurs in nature. Costerton, et al.[42] showed that dental plaque is the result of bacteria sticking to the tooth surface and to each other due to a glycocalyx (polymer) coating.

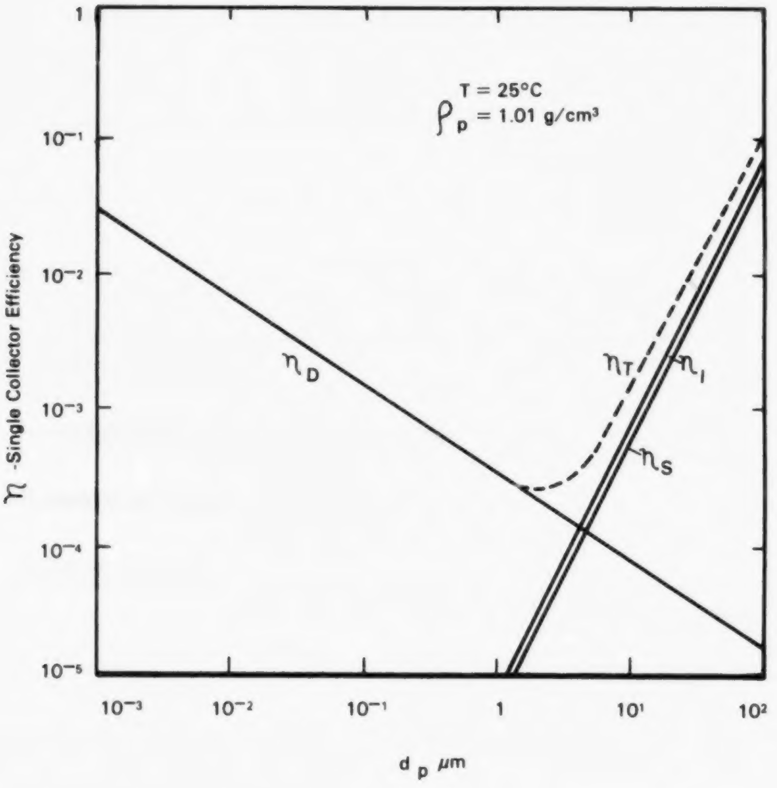


Figure 9. Single collector efficiency as a function of suspended particle diameter.

Process Selection

It is recognized that high turbidity waters are readily treated in a conventional water treatment plant (Fig. 4) while direct filtration (Fig. 5) is potentially applicable to the treatment of low turbidity waters. The analysis that follows describes a dimensionless product called the coagulation effectiveness factor. This coagulation effectiveness factor will be used to establish guidelines for the design and performance of coagulation-flocculation systems.

Let us examine the design of flocculation basins in conventional plants. Camp[33] introduced the dimensionless product, $G\bar{t}$, and indicated that good flocculation can be expected in a basin when this product is in the range of 10^4 to 10^5. This product reflects the influence of two physical parameters - velocity gradients provided by mechanical mixing to induce particle collisions and detention time to permit floc formation. We assume that chemical pretreatment has been successful, and that there are sufficient particle numbers either in the raw water or introduced by the coagulant for flocculation to be efficient. Clearly, if insufficient coagulant has been added for particle destabilization or if there are insufficient particle numbers for collisions, then poor floc formation will result with poor separation of solids in the sedimentation tank. O'Melia[43] has indicated that we must consider other parameters in addition to Camp's dimensionless product to account for particle destabilization and particle number concentration.

Coagulation Effectiveness Factor—

Using the orthokinetic flocculation equation (Equation 4) and including a parameter α, we get:

$$\frac{dN}{dt} = -\frac{2}{3}\alpha G d^3 N^2 \tag{16}$$

The parameter α is a colloid stability factor which reflects then the success we have in adding coagulant to destabilize particles. It may also be viewed as a collision efficiency factor or sticking factor, since it represents the fraction of the total number of particle collisions that are successful in producing aggregation. Particles which are completely stable (no coagulant addition) would have α values approaching zero while complete particle destabilization (all particles stick upon colliding) would correspond to a value of 1.0.

Introducing the expression for the floc volume fraction (ϕ), which is defined as the volume of colloidal particles per unit volume of suspension, yields:

$$\phi = \left(\frac{\pi d^3}{6}\right) N \tag{17}$$

Since we can assume particle volume is conserved in a flocculation tank we can substitute Equation (17) into Equation (16) which yields:

$$\frac{dN}{dt} = -\frac{4\alpha\phi G N}{\pi} \tag{18}$$

Integration of Equation (18) for the boundary conditions $N = N_O$ at $t=0$, and N_t at any time t results in:

$$N = N_O e^{-\frac{4\alpha\phi G t}{\pi}} \tag{19}$$

Setting t as the detention time ($\bar{t}$) of the flocculation process shows that the performance of the coagulation-flocculation process should be evaluated from the dimensionless product ($\alpha\phi G\bar{t}$) – coagulation effectiveness factor.

Of course this is a simplification, since we assumed a monodispersed particle system; nonetheless, coagulation effectiveness will be considered using this product, since it considers not only $G\bar{t}$ (Camp's product), but also α (particle destabilization) and ϕ (particle volume fraction). Three cases are presented to illustrate the significance of the coagulation effectiveness factor.

Case 1: Raw water containing humic particles at a concentration of 5 mg/L. This suspension was previously described as Case 1. It will be assumed that the particles have been destabilized with either a cationic organic polyelectrolyte or by positively charged dissolved aluminum hydrolysis products. Characteristics of the particles follow:

ρ = 1.01 g/cm^3
d_O = 0.021 μm (initial diameter)
N_O = 10^{12} particles/cm^3 (initial number)

For these particles to flocculate to a size (say, 2.1 μm) in which orthokinetic flocculation is applicable requires a decrease in particle number concentration. Fig. 6 shows that an increase in a particle size of two orders of magnitude decreases particle number concentration by six orders of magnitude (N is proportional to $1/d^3$). At this point ϕ would be 4.95×10^{-6}. We will assume α equal to 0.5 meaning half the collisions are successful in particles sticking. Using typical values for G and $\bar{t}$ for conventional flocculation basins of 20 sec^{-1} and 45 min, respectively, results in:

$$\alpha\phi G\bar{t} = 0.5\ (4.95 \times 10^{-6})\ (20)\ (45)\ (60) = 0.13$$

Note that Camp's product is 54000, which would be considered an acceptable design.

Case 2: Low turbidity water containing clay-type particles which has also been destabilized in the same way and to the same degree as Case 1 - i.e., α equal to 0.5. The suspension previously presented as Case 2 is used.

$d = 1.6\ \mu m$ and $\rho = 2.5\ g/cm^3$
Solids concentration = 5 mg/L (turbidity of 7-8 NTU)
$N = 10^6$ particles/cm^3
$\phi = 2 \times 10^{-6}$
$\alpha\phi G\bar{t} = 0.5\ (2 \times 10^{-6})\ (20)\ (45)\ (60) = 0.05$

Again note that Camp's product has been maintained at a value of 54000.

Case 3: High turbidity water containing clay-type particles which has been destabilized in the same manner and degree as the previous cases. Characteristics of the particles follow:

$d = 1.6\ \mu m$ and $\rho = 2.5\ g/cm^3$
Solids concentration = 100 mg/L (turbidity of say 160 NTU)
$N = 1.87 \times 10^7$ particles/cm^3
$\phi = 4 \times 10^{-5}$
$\alpha\phi G\bar{t} = 0.5\ (4 \times 10^{-5})\ (20)\ (45)\ (60) = 1$

The turbid water of Case 3 is easy to treat by conventional treatment. The coagulation effectiveness factor has a value of 1. Values of about 1 or greater would indicate that coagulation-flocculation is effective. For conditions illustrated by Cases 1 and 2 in which the coagulation effectiveness factor is 0.1 or less indicates that these waters would be difficult to treat by conventional coagulation processes even though Camp's dimensionless product of $G\bar{t}$ would indicate that the flocculation basin is adequately designed.

Further development of the above concepts leads to the following recommendations. The product, $G\bar{t}$, represents the engineer's design of mixing equipment (G) and size ($\bar{t}$) of the flocculation basins. These factors influence greatly capital costs of design. The product, $\alpha\phi$, takes into account coagulant selection and dosage (α) and particle concentration (ϕ). Both factors are influenced by raw water characteristics and may be altered by plant operation. A water plant operator can treat the waters described in Cases 1 and 2 by adding particles (increasing ϕ) through the addition of a coagulant aid (clays) or by using metal salts as coagulants under conditions in which a metal precipitate is produced ("sweep floc"). In addition, choice of coagulant and dosage may improve α. The product, $\alpha\phi$, may be increased by plant operation, and therefore influences operating costs.

Another option is the use of solids contact flocculation-sedimentation basins (upflow tanks with a sludge blanket), which produces a high floc volume fraction as well as long solids detention times.

Jar Tests and Direct Filtration—

Jar tests are used to evaluate the destabilizing ability of various coagulants, to choose dosages, and to evaluate the effects of coagulant aids. In spite of their widespread use, jar test experiments are often criticized as being inadequate in predicting coagulant dosages for actual water treatment plants. Perhaps much of the criticism is due to a lack of understanding of what information jar tests provide.

Examining the coagulation effectiveness factor ($\alpha\phi G\bar{t}$), we see that in conventional treatment a number of parameters influence overall performance including: coagulant type and dosage which affect α, floc volume fraction (ϕ), mixing conditions of flocculation (G), and detention time ($\bar{t}$). The information obtained from jar tests is limited by the fact that they are batch tests and therefore cannot be expected to duplicate the continuous flow mixing conditions or fluid flow patterns of an actual plant. Thus, jar test conditions are standardized with respect to mixing intensity and times of flocculation and settling.

The jar test provides us with information about the destabilizing ability of a coagulant. In other words we can compare coagulants, and for a particular coagulant choose a dosage at which the particles have been destabilized to the greatest degree ($\alpha \rightarrow 1$) - i.e., coagulant dosage at which the particles are most sticky. The kinetics of flocculation as affected by ϕ, G, and $\bar{t}$ must be taken into account in applying jar test results to actual practice.

Consider the jar test data from Glaser and Edzwald[44] in the top of Fig. 10. The raw water contained 5 mg/L humic acid and the humic matter was destabilized with the cationic polyelectrolyte PEI-1000, polyethylenimine with a number average molecular weight of 50,000 to 100,000. The jar test data indicate that 3 mg/L is the best destabilization dosage, or the dosage at which the particles are most sticky. Dosages below and above this optimum dosage indicate underdosing and overdosing, respectively. The results of three filter experiments are shown at the bottom of Fig. 10, in which there was continuous feed of polymer at the dosages indicated. A polymer precoat of the sand media was used prior to filtration. Using the optimum jar test dosage of 3 mg/L resulted in almost complete removal of the humic acid (based on absorbance measurements at 420 nm). Dosages which the jar test predicted to be an underdose (0.5 mg/L) or an overdose (10 mg/L) resulted in unsatisfactory filtration performance.

If we consider that a filter operates, after an initial period, by collection of particles on previously retained particles, then the jar test must be able to select coagulant dosages for direct filtration. This is because the jar test tells us what dosage the particles will best stick together regardless of whether the particles stick together in a beaker (jar test) or stick to each other in a filter bed.

ORGANICS REMOVAL: CONCEPTS

This section is organized as follows. First, a summary of the physical and chemical properties of humic substances is presented. Second, knowledge on the coagulation of color or humic substances is examined with a view to describing the factors affecting the stability of humic materials and identifying the physical and chemical parameters which affect their removal from water supplies. Finally, recent work on the application of direct filtration to removing color and THM precursors is reviewed.

Humic Substances

Humic substances are amorphous, acidic, predominantly aromatic, hydrophilic, chemically complex macromolecules consisting of a complex mixture of naturally occurring organics, and are responsible for the natural color imparted to waters. A model humic compound, presented in Fig. 11, shows that part of the molecule has an amorphous mass of polyhetero condensate associated with certain functional

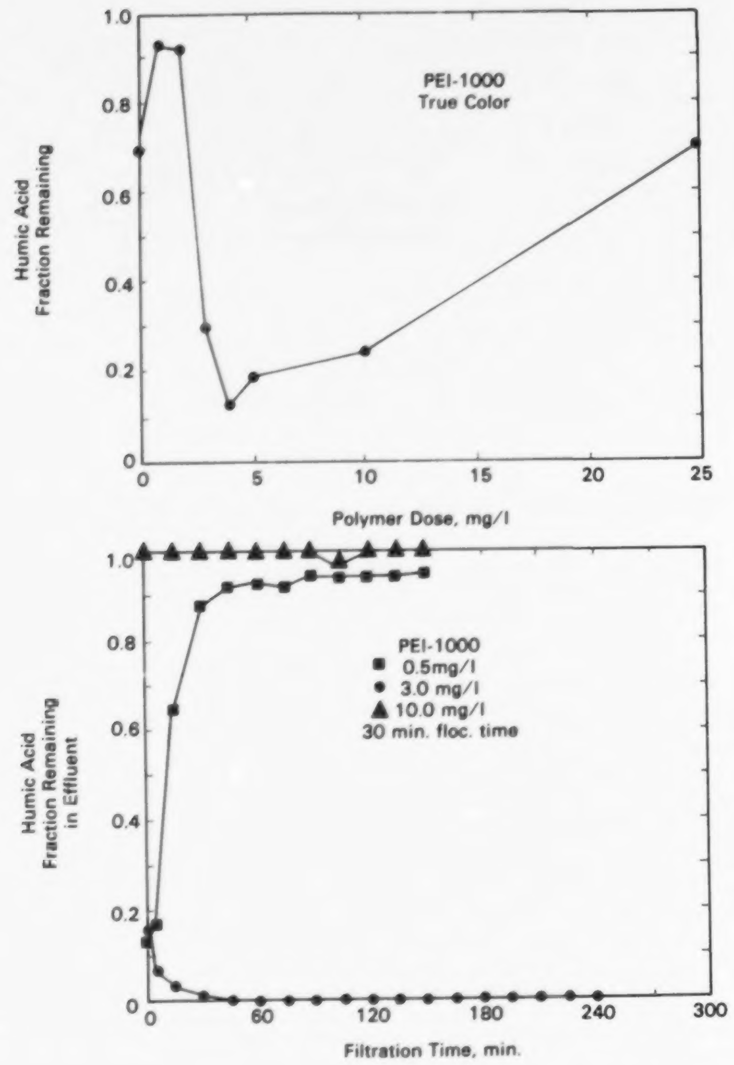


Figure 10. Comparison of jar test results with filter performance (Filtration conditions: 5 mg/L humic acid in raw water, pH 6, filtration rate 2 gpm/ft^2, 0.6 mm sand, bed depth of 14 cm) (After Glaser and Edzwald[44]).

groups. The terminology and much of our knowledge pertaining to humic substances comes from the field of soil science. Classification of the fractions of humic material has traditionally been based on the solubilities of three main fractions as follows: (1) humic acid (HA), which is soluble in alkali but insoluble in acid; (2) fulvic acid (FA), which is soluble in both alkali and acid; and (3) humin, which is insoluble in both

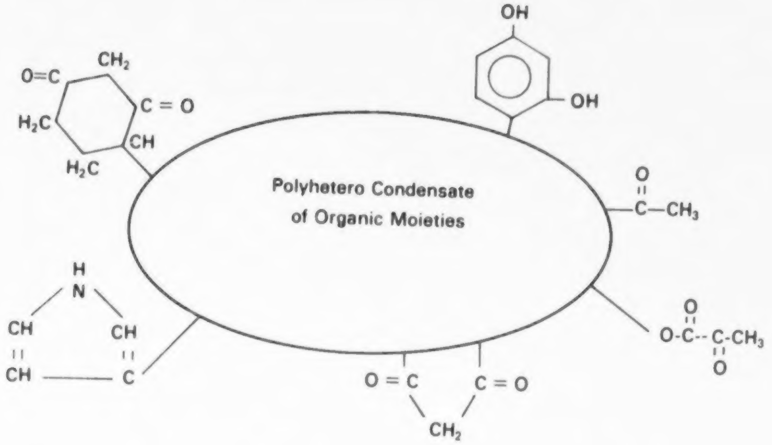


Figure 11. Model humic compound (From Trussell and Umphres[12]).

alkali and acid. Humic matter in natural waters may be soil derived or may be produced within the water body. The composition of aquatic humic matter would depend on the local biota. The color that we observe is due to the absorbance of light by these substances.

The three humic fractions are structurally similar, but differ in elemental analysis, functional group content, and molecular weight distribution[45]. A summary of the major elements typically found in humic and fulvic acids is presented in Table 5. Fulvic acids contain more oxygen but less carbon and hydrogen, and have a higher content of oxygen containing functional groups (COOH, OH, C=0) per unit weight. Nitrogen may be an impurity, although degradation of protein matter would explain its presence.

Humic substances contain the following functional groups in varying amounts: carboxyl, phenolic, alcoholic, methoxyl, carbonyl, ether, and ester. The molecular weight of humic substances is normally considered to range from the hundreds to tens of thousands. The molecular weight distribution of fulvic acids is much less and may be considered as being from about 200 to 10,000. Humic acids are considered as a higher molecular weight fraction. For the pH conditions of most natural waters, humic materials are negatively charged macromolecules or anionic polyelectrolytes in which the carboxyl and phenolic functional groups affect their colloidal stability. As the pH increases above say about 5, the negative charge and therefore stability of humic materials increase due to dissociation of the functional groups. In addition, the configuration of the humic molecule in water will depend upon ionic strength and pH. An extended configuration would be expected with increasing pH as a result of repulsion between negatively charged functional groups.

Coagulation of Color

Work in the 1960's highlighted key water treatment operational parameters affecting the coagulation of humic substances or color with alum and iron salts[47-49]. These parameters include: the concentration of humic material in the raw water, coagulant dosage, pH, and the influence of particulates (turbidity). Recent work[50-52] has summarized the state-of-the-art and examined mechanisms of coagulation.

Table 5. Elemental Analysis of Humic and Fulvic Acids (From Ref.[46])

Element	Percentage, dry ash-free weight	
	Humic acid	Fulvic acid
C	50-60	40-50
H	4-6	4-6
O	30-35	44-50
N	2-6	<1-3
S	0-2	0-2

In summary, the coagulation of humic substances with inorganic coagulants such as alum can be accomplished through two mechanisms of destabilization - charge neutralization or precipitation. Destabilization may be accomplished by charge neutralization resulting from specific chemical interaction between positively charged aluminum species and the negatively charged groups on the humic colloids. Destabilization by this mechanism would be accomplished over a narrow pH range (pH 4 to 6) and a stoichiometric relationship between the raw water humic concentration and the optimum coagulant dosage would be observed. Humic substances can form water-soluble and water-insoluble complexes with metal ions. As the alum dosage is increased precipitation may occur; however, destabilization via this mechanism may include incorporation of humic material within aluminum hydroxide floc or co-precipitation as aluminum humate. The effect of pH on the coagulation of humic acid with alum is shown in Fig. 12. High alum dosages are required above pH 6.

The stability of color colloids differs from that of particles such as clays. Consequently, it has been found that the optimum pH for removal of natural organics is also different [52,53]. Coagulation of humic substances with hydrolyzing metal ions is favored at acidic pH conditions, pH 5 to 6 with alum and pH 4 to 5 with ferric chloride. Coagulation at these pH conditions, which relies principally on charge neutralization, would mean that greater coagulant dosages would be needed due to the presence of turbidity. Another alternative is to coagulate at higher pH conditions with enough coagulant added to achieve a "sweep floc" effect in which the humic material is incorporated in the floc.

An effective method for the removal of humics involves the use of high molecular weight polymers as coagulant aids with alum[51-54]. Excellent color removal is achieved over the pH range of 4.5 to 6 as shown in Fig. 13. For best results, the alum is added first followed shortly by polymer. Destabilization mechanisms are charge neutralization by positively charged aluminum species and interparticle bridging of the floc by the polymers. Excellent solids-liquid separation is achieved as the floc settles rapidly.

Cationic polyelectrolytes used as the sole coagulant can destabilize humic substances[44,55,56]. Glaser and Edzwald[44] reported on the coagulation of humic acid using a homologous series of cationic polyelectrolytes. A stoichiometry was observed between the raw water humic acid concentration and the optimum polymer dosage for destabilization. They proposed a model for destabilization and aggregation which is illustrated schematically in Fig. 14. The destabilization of the humic acid is highly charge dependent, and is accomplished by neutralization of the anionic functional groups on the humic macromolecule by cationic polymer functional groups. Aggregation can occur as humic and cationic polymer molecules are cross-linked in a random configuration to form floc.

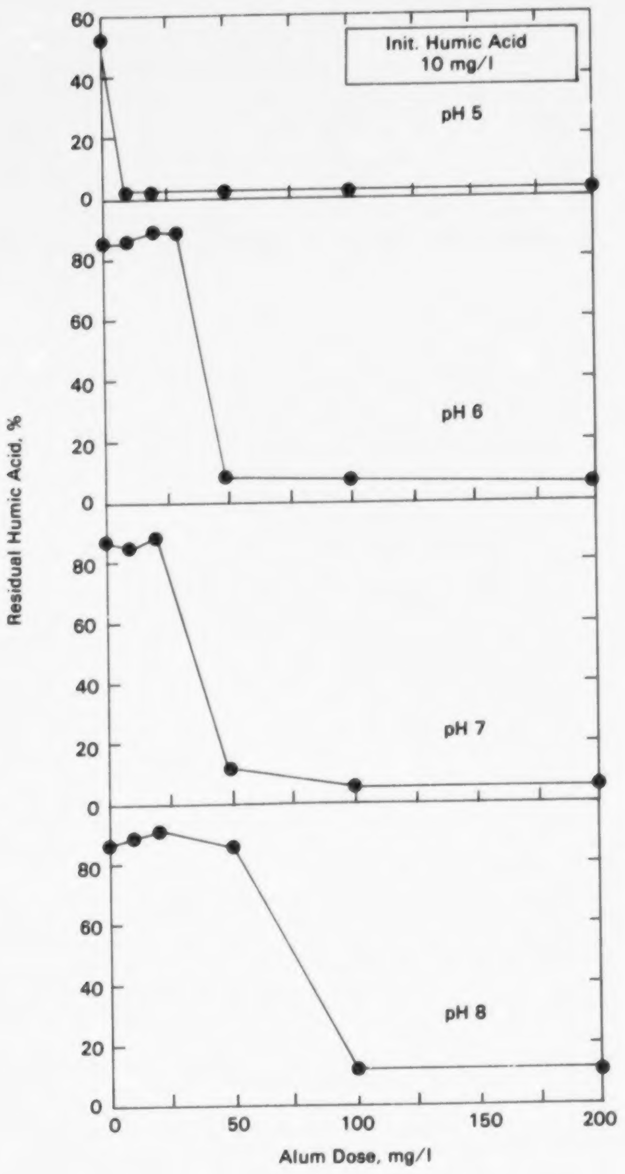


Figure 12. Effect of pH on the coagulation of humic acid with alum (After Edzwald[51]).

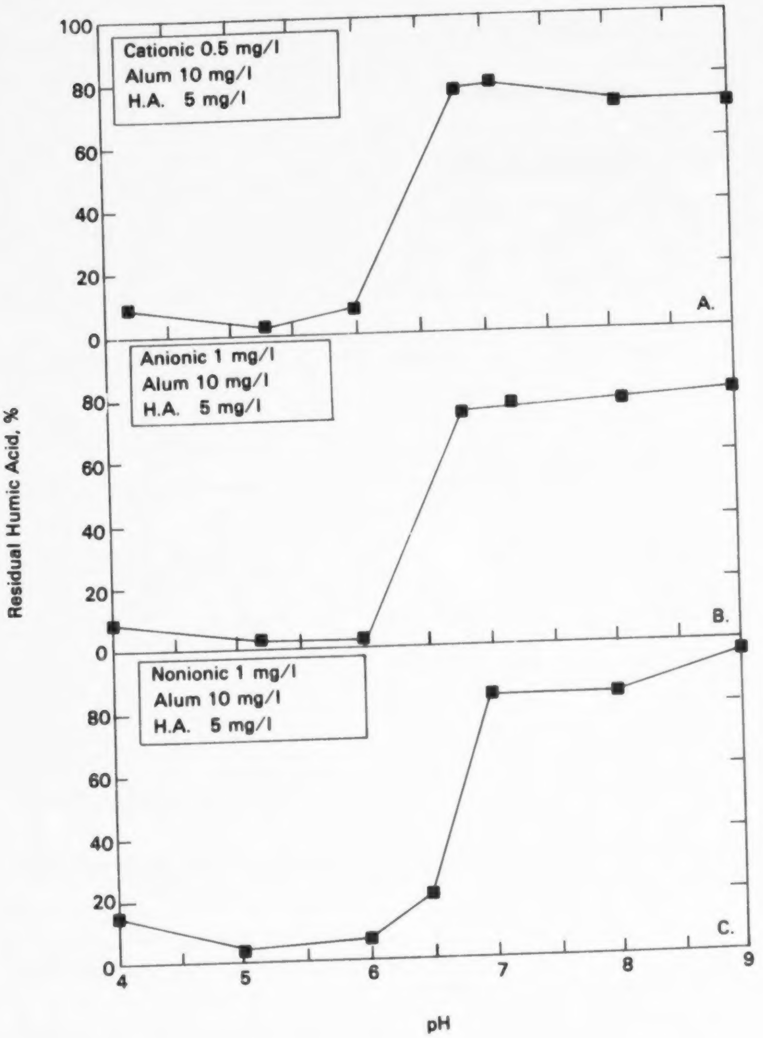


Figure 13. Effect of pH on the coagulation of humic acid using alum and high molecular weight polymers (After Edzwald[15]).

Direct Filtration

Direct filtration offers advantages over conventional treatment in lower capital costs and possibly, lower operating costs. In spite of the potential advantages, there is very little information on the use of direct filtration for treating low turbidity, colored water supplies. Some results of recent pilot plant research by the author are presented here.

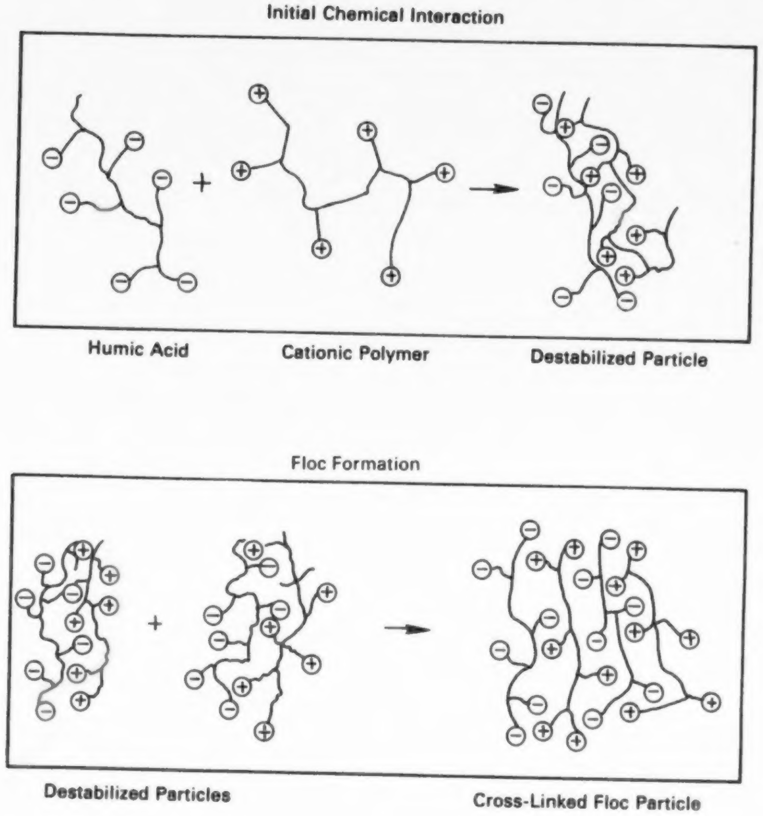

Initial Chemical Interaction
Humic Acid
Cationic Polymer
Destabilized Particle
Floc Formation
Destabilized Particles
Cross-Linked Floc Particle

Figure 14. Schematic representation of the destabilization and aggregation of humic acid by polyethylenimine (After Glaser and Edzwald[44]).

Glaser and Edzwald[44] investigated the use of direct filtration for color removal using both a low turbidity, colored river water and a synthetic water containing humic acid. Significant findings were:

- Excellent color removal was achieved as illustrated in Fig. 10; also, low filter effluent turbidities were observed.
- Polymer dosages for filtration can be selected from jar test experiments. As shown in Fig. 10, underdosing and overdosing in the jar test produce the same phenomena in filtration.
- For low turbidity waters containing natural color in which the particles are submicron in size, a brief flocculation period prior to filtration reduces the head loss across the filter bed when compared to direct filtration without flocculation.

The limited data on THM precursor reduction by direct filtration in treating colored waters are based on two pilot plant studies[19,57]. In both studies a cationic polyelectrolyte was the only destabilizing chemical used. Scheuch and Edzwald[57] found reductions in THM precursors (measured by the reduction achieved in $CHCl_3$

formation potential between raw and filtered waters) of 50 to 60% for humic acid waters and approximately 40% for a low turbidity, colored river water.

The EPA's pilot plant facilities were used in a study[19] employing dual media filters and filter rates of 4.9 m/hr (2 gpm/ft^2) and 12.2 m/hr (5 gpm/ft^2). Filter experiments utilized a low turbidity water spiked with humic acid to produce color. Excellent results were achieved in terms of classical measures of filtration performance: effluent turbidities less than 0.3 NTU, effluent apparent color less than 5 Pt-Co units, and moderate head loss development. Total trihalomethane formation potentials were reduced by approximately 50 percent. Typical results are shown in Figs. 15 and 16.

ORGANICS REMOVAL AND THM REDUCTION: WATER TREATMENT PRACTICE

In recent years there have been numerous seminars and publications on controlling THM formation and removing organics, particularly THM precursors. Each month additional articles are published in scientific journals and additional EPA publications appear. What may be gleaned from the voluminous information already available to assist water treatment professionals in solving the problem without increasing capital costs of new or existing plants? There are several considerations. The practice of prechlorination should be evaluated at many water treatment plants. Common practice is to add chlorine at high dosages so that free residual chlorine is measured at the end of the plant. For many waters which contain humic substances, most of the chlorine demand is due to the humic material so that chlorine is being wasted by converting the humics to chlorinated organics. It would be better to remove the humic material prior to chlorination, thus reducing the chlorine demand and THM formation as well as realizing the cost savings resulting from using less chlorine. The need for prechlorination of water supplies on a continuous basis to control slime growths in sedimentation basins and filters should be re-examined. This practice may be necessary only on an intermittent basis; during the winter season it might be discontinued altogether. Another option is to use an alternative predisinfectant such as chlorine dioxide. The latter does not produce THMs unless chlorine resulting from generation of the chlorine dioxide is present. Chlorine dioxide has other advantages in that it can oxidize reduced iron and manganese, control slime growths, and destroy taste and odor producing compounds. Oxidants such as chlorine dioxide are discussed in another chapter. In summary, some economical options are: reduce the prechlorination dosage, omit prechlorination, and optimize the removal of organics by coagulation and sedimentation prior to chlorination.

Two cases from water treatment plant practice are presented below to illustrate some simple principles regarding THM formation and control. The first case involves moving the point of chlorination at the Durham, N.C. water treatment plant. This case is taken from the published work of Young and Singer[58]. The second case involves work of the author at the Canton, N.Y. water treatment plant.

Durham, N.C.

The raw water source for Durham is an impounded reservoir, Lake Michie. The water treatment plant is a conventional plant employing liquid alum addition to the rapid mix basins for coagulation. A nonionic polymer is added ahead of the dual media filters as a filter aid. The plant was sampled thirty times between July 1976 and January 1977 while prechlorination was being practiced by addition of chlorine to the rapid mix basins. Over this period, the average raw water non-volatile total organic carbon (NVTOC) was 5.1 mg/L, the average chlorine dosage was 5.8 mg/L, and the average $CHCl_3$ concentration of the finished water was 129 μg/L. In January

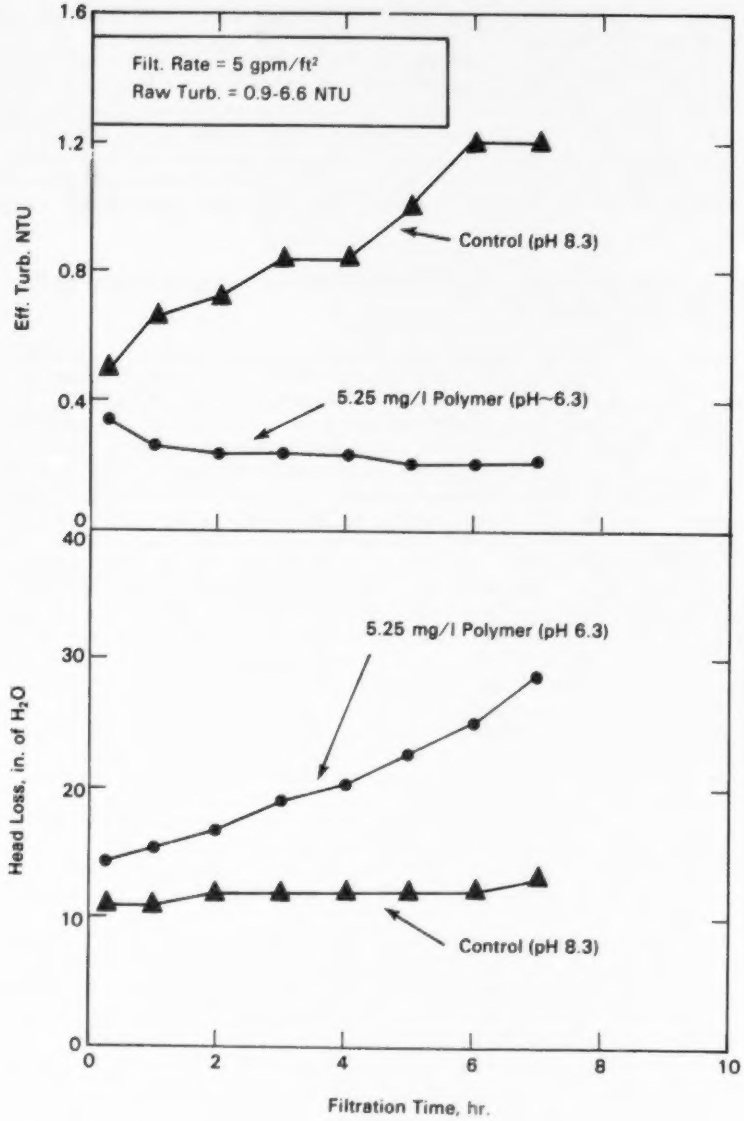


Figure 15. Turbidity and head loss data for spiked humic acid-gravel pit water, direct filtration (Pilot plant operated at pH conditions indicated).

1977, prechlorination was stopped and the point of chlorination was moved to a point following sedimentation. Over the next few months, the average raw water NVTOC was 5.7 mg/L, but the chlorine dosage was reduced to 3.5 mg/L and the average $CHCl_3$ concentration of the finished water was 77 μg/L. Temperature effects

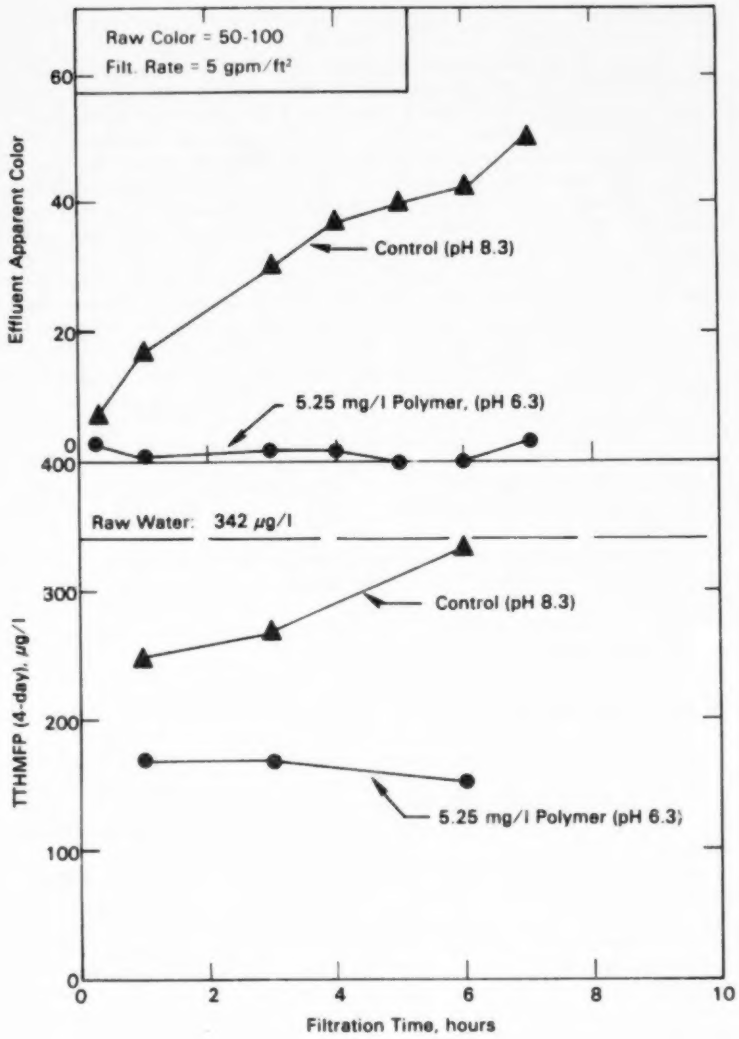


Figure 16. Apparent color and TTHMFP data for spiked humic acid-gravel pit water, direct filtration (Pilot plant operated at pH conditions indicated, TTHMFP data for pH 8.3).

were discounted so that the 40 percent reduction in $CHCl_3$ was attributed to the change in the location of chlorination, and by the fact that the plant removed 35 percent of the total organic carbon. An important point is that not only was the $CHCl_3$ reduced to below 100 μg/L, the reduction in the amount of chlorine added resulted in a savings of $50/day in plant operation.

Canton, N.Y.

The Canton, N.Y. water treatment plant is a conventional plant employing coagulation, flocculation, tube settlers, and filtration. Alum and a nonionic polymer are used in coagulation-flocculation. The water source is the Grasse River, a raw water supply of low turbidity, but high color. The plant was monitored during a period of spring runoff (April). In the monitoring program, total trihalomethane formation potential (TTHMFP@ pH 7.5, 20°C) of the raw water as well as Inst TTHMs and Term TTHMs throughout the plant were measured to evaluate process performance. The 7-day TTHMFP of the raw water was 537 μg/L. Its formation curve was shown earlier in Fig. 3. Samples for Term TTHM were buffered at pH 7.5, spiked with 15 to 20 mg/L chlorine, and held 7 days at 20°C. These chlorine spiked Term THM samples served as a basis for evaluation of precursor removal.

Fig. 17 shows THMs through the plant and various surrogate parameters for THM precursors. The water temperature through the plant was 5°C to 6.5°C and a free chlorine residual was maintained as shown in Fig. 18 with a prechlorination dosage of only 1 mg/L. The total organic carbon was reduced from 6.3 mg/L to 2.1 mg/L, a 67 percent reduction. The Inst THM of the finished water was 51 μg/L due to the low temperature, low chlorine dosages, and brief chlorine contact period in the plant. Comparing the 7-day raw water TTHMFP (537 μg/L) with the 7-day finished water Term TTHM (168 μg/L) shows good reduction of THM precursors--69 percent reduction. Ultraviolet (UV) absorbance was reduced by 83 percent through the plant.

Turbidity data for the plant showed, as did the TOC and Term THM data, that the filters were removing most of the floc and organics. In effect, the plant was being operated much like a direct filtration plant. Other data indicate that when the water temperature is warmer, the efficiency of the sedimentation tank improves for removal of both turbidity and organics[59].

FINAL COMMENTS

Much is known about the coagulation of turbidity. During the 1970's the problem of organics in drinking water stimulated research on the coagulation and removal of organics from drinking water supplies, particularly naturally occurring organics and THM precursors. Additional research is needed. A description of research needs follows.

Fundamental studies on the coagulation of organics are needed. These studies should include well-characterized organic materials - e.g., humic and fulvic acids of known molecular weight distributions - as well as research with actual waters. It is important, however, that the organic material be characterized so that mechanisms of coagulation can be elucidated and so that the results could be interpreted for their applicability to appropriate water supplies. The research should examine the use of alum, iron salts, and polymers in combination with the inorganic coagulants. Optimum coagulation conditions should be identified such as pH and coagulant dosages as a function of the nature of the organic material in the raw water and the organic concentration. Mixing conditions for the addition of the coagulants should be studied, in particular when polymers are added as coagulant aids. These studies should determine the removals of organics and THM precursors that can be accomplished by coagulation.

Many water utilities obtain their water supplies from sources of low turbidity and currently practice only disinfection. These utilities are faced with the problem of adding additional treatment to ensure that they meet the one NTU turbidity standard, but must now also consider the ability of the proposed treatment to remove THM precursors. Typical options would be a conventional water treatment plant or direct filtration. While there have been some pilot scale direct filtration studies which have investigated the ability of direct filtration to remove organics and THM

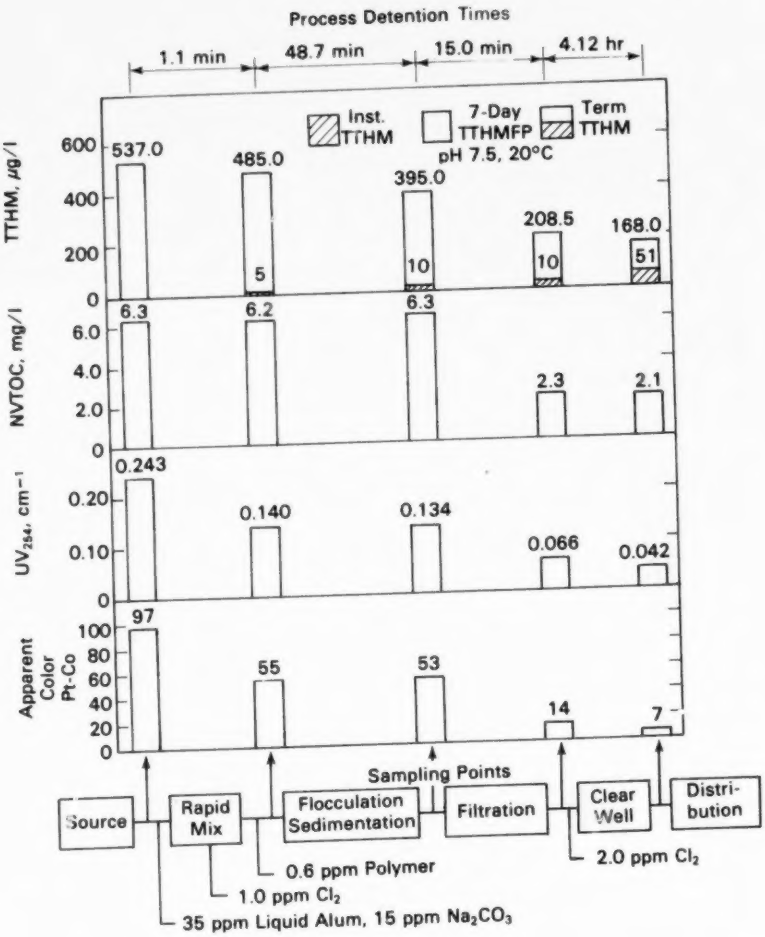


Figure 17. Monitoring of the Canton, NY water treatment plant in April (flow 2.8 MGD, water temperature through plant 5 to 6.5°C).

precursors, additional research is needed with surface waters on both a larger pilot scale and full plant scale. There are many direct filtration plants in the United States which could be examined for their ability to remove THM precursors.

Finally, surrogate measurements are needed for characterizing the problem of organics in raw water supplies and for use as process control parameters in water treatment plants. The total organic carbon content of a water may be measured, but this is a collective measure as it measures both THM precursors and non-precursors. However, we can definitely expect, as pointed out in this chapter, a relationship between the organic content of a water and its trihalomethane formation potential. Two observations about total organic carbon measurements are important. First, there is a scarcity of data on the total organic carbon (TOC) content of untreated and

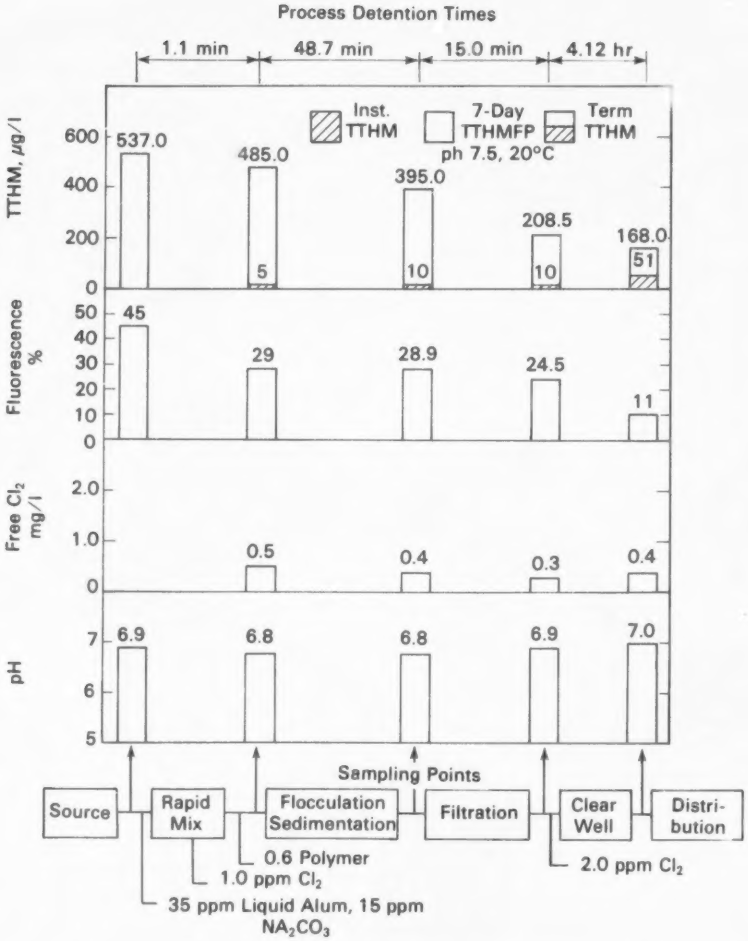


Figure 18. Monitoring of the Canton, NY water treatment plant in April (Flow 2.8 MGD, water temperature through plant 5 to 6.5°C).

especially treated waters. Most natural waters have TOC levels in the 1 to 20 mg/L range, although a particular water supply can vary considerably over the year. For example, the Grasse River which was mentioned earlier (Fig. 3) has low TOC concentrations (2.75 mg/L) in February during ice-cover, higher values (6.3 mg/L) in April during spring runoff, while the highest TOC concentrations (12.6 mg/L) occur in the summer following heavy rains in the watershed. Data are needed on the seasonal variation of TOC in raw water supplies and the ability of water treatment plants to remove organic matter. Second, instrumentation for measuring organic carbon is expensive. Small water utilities will be unable to afford such instrumentation. Thus there is a need for a surrogate measurement of organics in water. UV absorbance is a promising surrogate measurement[60,61]. The measurement can be made easily, rapidly, and inexpensively, and is thus advantageous in water treatment processes for monitoring dissolved organics. Sontheimer et al.[61] have reported on using UV absorbance at 254 nm in water treatment practice for this purpose. For a particular water supply, correlations could be developed between not only total organic carbon and trihalomethane formation potential (THMFP) or Term THMs, but also between UV (254 nm) absorbance and THMs. This might be done for both raw and treated waters.

Traditionally, color has been measured in water treatment plants by comparing samples visually with platinum-cobalt standards. The measurement is rapid and easy, but has many drawbacks. Particulates must be removed from the sample to get so-called true color readings. In addition color intensity is affected by pH with greater intensity at higher pH. The lack of accuracy with the visual comparison method and the lack of standardizing conditions such as pH makes it difficult to compare color readings of one water treatment plant or laboratory with that of another. Since color could serve as a surrogate measure of TOC, and thus THM precursors, simple color measurements could serve as a rough monitoring parameter in water treatment. There is a need, however, to replace the visual comparison method with a spectrophotometric measurement at a standard wavelength and pH.

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ADSORPTION OF ORGANIC SUBSTANCES IN DRINKING WATER

Francis A. DiGiano, PhD

INTRODUCTION

Early History

Throughout the modern history of water treatment, adsorption has been used for removal of taste and odor causing compounds. Compounds associated with taste and odor derive from chlorinated phenols and by-products of algal and vegetable matter decay. In the case of chlorinated phenols, their precursor, phenol, may be adsorbed prior to chlorination. Adsorption has also found application following chlorination for removal of chlorinated aromatic compounds and excess free or combined chlorine which may be present, for example, after treatment of more highly contaminated surface waters.

The adsorbent of choice has traditionally been powdered activated carbon (PAC). This is so because it does not require significant capital investment and because it is used only when taste and odor problems arise, e.g. seasonally. The point of addition of PAC is usually in the chemical coagulation step of the conventional water treatment plant.

As an historical note, Rosenau[1], in his classic text *Preventive Hygiene and Medicine* (Sixth Edition, 1935) heralded the addition of PAC as a great advance in water treatment. He pointed out that PAC was the accepted adsorbent despite the fact that Baylis[2], a well-known researcher, had earlier demonstrated the effectiveness of granular activated carbon (GAC) for removal of taste and odor and for dechlorination in large-scale experiments at the Chicago water works. Rosenau stated that GAC is not the adsorbent of choice because "such a practice would involve considerable initial outlay for material and its frequent removal or regeneration when it became charged with adsorbed impurities." Today, this same argument is being used to oppose proposals to control synthetic organic contaminants by GAC. This contemporary argument will be discussed later in greater detail.

The 1960's: A Growing Interest

Although the historical functionof PAC as an adsorbent of taste and odor compounds remains important today, the early 1960's brought recognition of the more general role of adsorption in removing organic contaminants. The specific classes of

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compounds of concern were the pesticides and the detergents. An attempt was made to measure trace organic contaminants collectively by passing the water sample through GAC, desorbing adsorbed compounds by treating the GAC with either chloroform or chloroform and ethyl alcohol, and finally weighing the extract to measure the organic compounds collected. This procedure takes advantage of the ability of granular activated carbon to adsorb a wide spectrum of organic contaminants, particularly those that are non-polar and slightly polar. Similarly, extraction in either chloroform or alcohol would selectively concentrate non-polar contaminants.

The ineffectiveness of conventional water treatment in removing organic contaminants can be illustrated by carbon-chloroform extractions (CCE) of raw and treated Missouri River water at Omaha, Nebraska during the period 1958-1962 (Table 1). These measurements showed that conventional treatment, consisting of coagulation (with PAC addition), sedimentation and filtration, was not removing compounds concentrated by the CCE procedure[3]. It must be emphasized, too, that not all organic compounds were being detected. Later surveys by the Organic Contaminants Committee of the American Water Works Association (AWWA) revealed that organic contamination, as measured by several different procedures, was a widespread problem[4]. Despite these findings, conventional United States treatment practice was not to be changed easily.

The 1970's: Evolving Public Policy

The American Water Works Association was concerned enough about organic contaminants in the early 1970's to expand the responsibility of its Research and Technical Practice Committee on Taste and Odor to include organic matter in general. The Committee cosponsored a special conference with the University of Illinois in 1973 to examine the growing problem of organic contamination[4]. By this time, approximately 100 organic contaminants, some thought to be toxic, had been identified in public drinking water supplies. The importance of controlling organic contamination by the adsorption process was stressed at this conference by Middleton of the U.S. Environmental Protection Agency (EPA). He recognized rather prophetically, however, that setting of "realistic and practical standards that can be justified and enforced" would be a problem. Nevertheless, Middleton questioned the widespread practice of delivering water to consumers from a polluted source without treatment which included activated carbon.

By the mid 1970's, a concern with organic contamination of drinking waters had blossomed into one of the leading issues of the water works industry. It was fueled by the National Organics Reconnaissance Survey (NORS)[5] and the National Organics Monitoring Survey (NOMS)[6], both conducted by the EPA. These surveys showed the ubiquitous nature of organic contamination and confirmed in factual detail the apprehensions expressed by environmental engineers and scientists in the 1960's. In addition to contaminants traced to industrial sources, special concern arose over the production of trihalomethanes (i.e., chloroform, bromodichloromethane, chlorodibromomethane and bromoform) in water treatment by the practice of chlorination.

The Safe Drinking Water Act of 1974 mandated the regulation of drinking water contaminants which "may have an adverse effect on the health of persons;" how to control these contaminants became a major question of the 1970's. In this regard, the control of trihalomethanes as a by-product of disinfection became a separate, identifiable problem. The EPA reported to Congress[7] in 1975 that although adsorption was a possible solution, its effective use for removal of trihalomethanes (THMs) and their precursors was limited by inadequate experience in use of the adsorption process. A large effort was therefore mounted to test and demonstrate the effectiveness of activated carbon, as well as alternative adsorbents, in controlling specific and

Table 1. Average Annual CCE* Concentration in Missouri River Water at Omaha[3]

Year	Raw Water	Tap Water
	CCE-ppb	
1958	35.7	45.2
1959	38.3	27.3
1960	37.7	24.5
1961	83.5	27.6
1962	40.2	33.5

ppb = parts per billion
*CCE is carbon-chloroform extract as measured by the high-flow carbon adsorption method (CAM-hf)

non-specific organic contaminants, the latter being measured by some overall parameter, such as, for example, non-purgeable total organic carbon (NPTOC).

As a result, emphasis on adsorption research shifted greatly. In the 1960's and early 1970's, interest was directed mainly to removal of residual organic contaminants in wastewater treatment. Now, the major focus is clearly on the problem of removing quite specific contaminants which were being found in very low concentrations in water supply sources. Promulgation of the Interim Primary Drinking Water Regulations in 1977 and the attempt in 1978 by EPA to promulgate yet another, more encompassing regulation[8] did much to shape development of the adsorption process as a part of water-treatment. GAC adsorption was the recommended method of controlling the six pesticides specified in the 1977 regulation[9]. This was not nearly as controversial as the proposed 1978 regulation which would have required that GAC, or its equivalent, be used on water supplies serving populations greater than 75,000 and believed to be subject to contamination by synthetic organic chemicals of industrial origin.

Observers may find it difficult to understand why the water works industry itself took the official position of opposing this regulation which seemed to offer greater protection to the public[10–12]. However, important questions had been raised concerning costs and effectiveness, and these needed to be answered if the process was to be accepted. The AWWA aired these issues at its national conferences and in its Journal. As a result, technical and management personnel have become far better informed than a decade ago about the details of the adsorption process and the experience with its use in several Western European countries.

Although the 1978 regulation requiring installation of the adsorption process was not promulgated, it heightened the interest of water utilities in adopting some method of controlling organic contamination. Should GAC adsorption be a recommended treatment method, its inclusion with coagulation, sedimentation, filtration, and disinfection could expand the concept of conventional water treatment practice. The most likely point of introduction of the adsorption process as a separate unit operation in the treatment scheme is after filtration, as shown in Fig. 1. At the same time, however, it should be noted that some plants have simply replaced the filter media (normally a mixture of sand and anthracite coal) by GAC and extended the bed depth so as to lengthen the time of contact with the water for better removal of the organic contaminants.

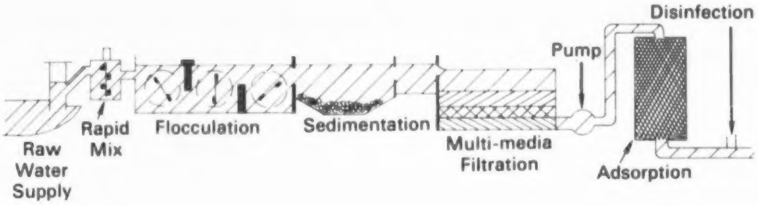


Figure 1. Modification of conventional water treatment practice to include the adsorption process.

PRINCIPLES OF ADSORPTION

General Considerations

Treatment by GAC, in contrast to PAC, requires a specific unit operation, commonly referred to as a contactor system. Fig. 2 depicts schematically the progression of the active adsorption zone down the length of the contactor and the resultant profile of concentration to be expected in the effluent. The capacity of the adsorbent to remove a contaminant is limited by physical and chemical factors which are related to the properties of both the adsorbent and the contaminant. As sorptive capacity becomes exhausted at any location in the bed, the active adsorption zone migrates further down. Eventually, there is very little sorptive capacity remaining and the contaminant begins to leak through the adsorbent bed. More and more leakage occurs as the final remnants of sorptive capacity are used. Finally, the bed becomes completely exhausted and no treatment is achieved. This pattern of increasing effluent concentration with operating time, or volume passed, is termed the breakthrough curve. Its shape and position are determined by principles of adsorption equilibrium and adsorption rate.

At some point in time along the breakthrough curve, the effluent quality deteriorates to an unacceptable level. This is termed the breakpoint concentration. The time of bed operation to breakpoint is commonly referred to as the service time.

Empty bed contact time (EBCT) is a commonly used design parameter. It refers to the hold-up time of water in the empty contactor volume, i.e. under the hypothetical condition of not being filled with the adsorbent. Because the contactor actually contains the adsorbent particles, which themselves occupy volume, the actual contact time is considerably shorter. The EBCT is calculated by dividing the volume of the contactor by the flowrate of water being treated. As EBCT increases, more water can be treated before breakthrough occurs because the volume of contactor, and thus the amount of adsorbent contained in the contactor, increases in proportion to the EBCT. The longer the EBCT then, the longer is the service time, or bed life.

Much of the adsorption process research of the early 1960's was stimulated by the U.S. Public Health Service's (USPHS) Advanced Wastewater Treatment Research (AWTR) Program. The emphasis here was on treating wastewater by adsorption to the extent that it could be reused. A classic example is the early research of Weber and co-workers on removal of detergents and pesticides[14,15]. This work resulted in a fundamental understanding of the adsorption process and provided the impetus for an expanded program of research on adsorption phenomena. Although the research was initially justified by a concern for reclaiming wastewater, the knowledge gained was applicable to removal of organics from any water source.

The early 1960's also saw practical evaluation of the adsorption process in water treatment. Workers at the USPHS's Robert A. Taft Sanitary Engineering Center were at the forefront of this research. Particularly significant was the work of Robeck, et al.[16] on adsorption of pesticides (lindane, dieldrin, DDT, parathion and

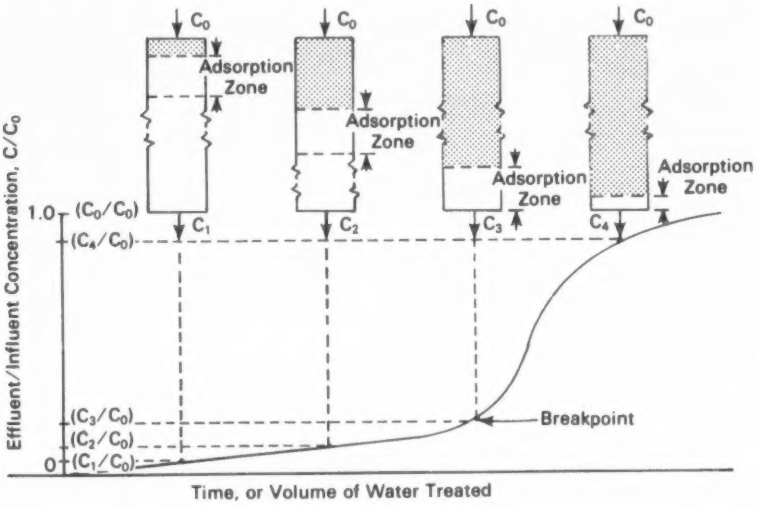


Figure 2. Schematic representation of the movement of the adsorption zone and the resulting breakthrough curve[13].

2,4,5-T ester) in the very low concentration range of interest (ppb levels) and under the practical conditions imposed by pilot plant treatment of the Little Miami River water. Some of their most significant findings dealt with the effect of competitive adsorption between trace contaminants and naturally present background organics compounds. As may be seen from Table 2, they noted that much larger dosages of PAC were required when pesticides were to be adsorbed from the Little Miami River water than from distilled water. Their findings gave practical significance to the theory of competitive adsorption as first discussed by Weber and Morris[17]. Competitive adsorption is also relevant to today's problem of evaluating the effectiveness of the adsorption process for removal of a wide variety of organic contaminants.

Another phase of research at the Robert A. Taft Center provided the first practical evaluation of GAC beds installed following conventional water treatment, i.e. after coagulation-sedimentation-sand filtration[16] (Fig. 3). It is clear from these results that GAC was very effective in removing pesticides. However, competitive adsorption was shown by Woodward, et al.[18] to cause displacement of organic compounds, these being measured by the CCE test. Occasional desorption actually yielded "negative" removals across GAC beds (denoted by black regions in Fig. 4), i.e. the effluent exceeded the influent concentration. These investigators noted that desorption corresponded to periods when the influent CCE levels were low. Again, the historical perspective gained by reviewing these observations of the early 1960's is useful in light of the fact that similar adsorption research questions were to be addressed in the 1970's.

Interest in adsorption led to GAC replacing sand in full-scale filters at the Nitro, West Virginia plant[19] in the mid-1960's. This is noteworthy because it marked the first time that specific design parameters of the adsorption system had actually been explored in pilot phase and at full-scale at an operating water treatment plant. The Nitro plant tests confirmed the intuitively obvious conclusion that the life of the adsorbent bed, i.e. its service time, should increase in direct proportion to the contact time provided by the bed (Fig. 5).

Table 2. **Parts per Million of Activated Carbon Required to Reduce the Pesticide Level in Distilled Water and in Little Miami River Water[16]**

Pesticide	Method	10 ppb*		1.0 ppb*	
		1.0†	0.1†	0.1†	0.05†
Parathion	JT‡	2.5	5	0.5	0.6
	P§	5	10	0.9	1.1
2,4,5-T ester	JT	2.5	17	1.5	3
	P	11	126	11	23
Endrin	JT	1.8	14	1.3	2.5
	P	11	126	11	23
Lindane	JT	2	12	1.1	2
	P	29	70	6	9
Dieldrin	JT	3	12	1.1	1.7
	P	18	85	7	12

*Initial level of pesticide.

†Pesticide level after treatment.

‡Jar test, in which pesticide is removed from distilled water by activated carbon alone, with a contact time of an hour.

§Plant treatment, in which pesticide is removed from river water by conventional treatment and activated carbon.

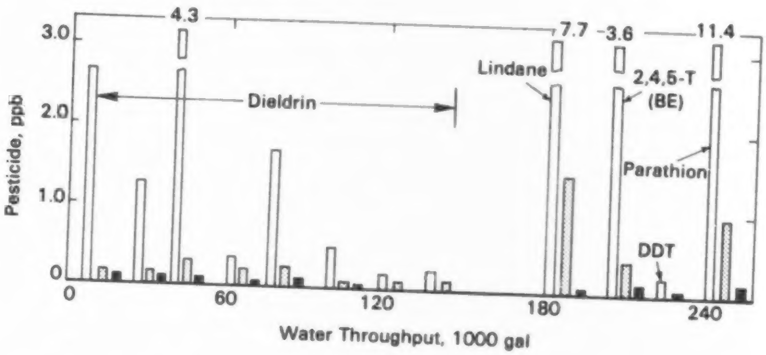


Figure 3. Passage of pesticides through carbon beds. The clear bars represent the initial stage; the cross-hatched bars, the result after passage through one bed; and the solid bars, the result after passage through the second bed[16].

Other design parameters were investigated at the Nitro plant. It was found that decreasing the particle diameter of the carbon increased bed service time, but that changing the velocity of the water through the bed, i.e. the application rate, had little effect (provided that the bed is lengthened so that contact time remains constant). Once again, sorption principles, which were being studied at the time by Weber and Morris[20] and Weber and Rumer[21], explained these observations. Their research showed that sorption rate is often controlled by diffusion of the contaminant within

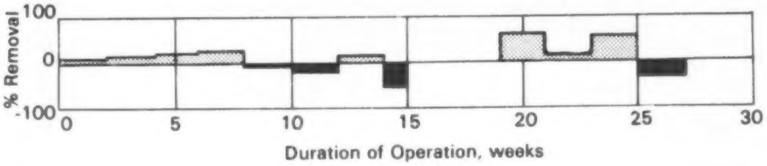


Figure 4. Effect of time on removal of carbon chloroform-extractable materials. The stippled area denotes removal by adsorption; the black, passage by desorption[18].

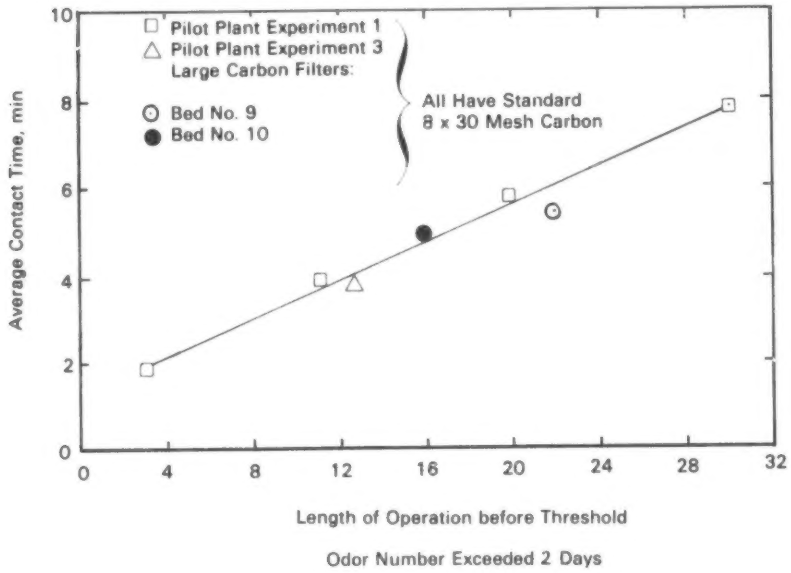


Figure 5. Effect of contact time on length of operation.[19]

the extensive internal pore structure of carbon particles. Internal diffusion, as it is termed, is therefore related to particle diameter. A smaller particle will promote faster adsorption, all else being equal, because the diffusional path length is shorter. Application rate, on the other hand, is unimportant because it only affects the rate at which the contaminant arrives at the external carbon surface and this in not the rate limiting step.

There were also differences in bed service time observed for each of the contaminants being removed by GAC at the Nitro plant. This suggested differences in sorptive behavior among these contaminants. The work of Weber and Gould[15] in the mid-1960's focused on quantifying such effects for related organic pesticides, detergents and phenol. As Table 3 indicates, they found notable differences in adsorption equilibrium. In this case the very well-known equilibrium model developed by Langmuir was used to quantify the maximum adsorption capacity, X_m, which

Table 3. Comparison of Langmuir Equilibrium Constants for Organic Pesticides and Selected Adsorbates[15]

Compound	X_m mg/gram	b liters/mg
2,4-D*	387	0.43
2,4,5-T†	448	0.58
Silvex	464	0.54
DNOSBP‡	444	0.72
DNOCHP§	500	0.55
Parathion	530	4.17
Phenol	103	1.15
Sulfonated 2-dodecylbenzene	139	12.82
1-Chloro-4-nitrobenzene	400	4.54

*2,4 dichlorophenoxyacetic acid
†2,4,5 trichlorophenoxyacetic acid
‡dinitro-o-sec-butylphenol
§dinitro-o-cyclo-hexylphenol

could be obtained and the partitioning of the contaminant between the solid adsorbent and the aqueous solution. The higher the value of the constant b in Table 3, the more strongly is the contaminant held to the adsorbent, even when it is present in very low concentrations.

A bridge, weak to be sure, was being built in the 1960's between adsorption theory and practice. Many questions were being raised simply by observing GAC bed performance at the Nitro plant and at other pilot plants. These necessitated a return to more fundamental studies to gain a better understanding of the process itself.

Use of Mathematical Models

The need for a mathematical model derived from principles underlying the adsorption process became increasingly apparent. However, the use of this device to predict the effluent concentration-time profile, i.e. the breakthrough curve, was virtually unknown in water treatment studies until Keinath and Weber[22] in 1968 presented their adaptation of principles hitherto applied in the chemical engineering field. The model serves several purposes: it facilitates convenient investigation of the effects which different parameters may have on the process without resorting to time consuming and expensive pilot plant tests; it also provides a guide to system design.

As Fig. 6 illustrates, Keinath and Weber[22] were actually quite successful in verifying their model using laboratory data obtained from GAC bed operation. Their model required that input data for adsorption equilibrium and rate be described by submodels. The output of the model could be used to show the effects of application rate , particle diameter, empty-bed contact time and feed concentration on the shape of the breakthrough curve (in this model, application rate is important because account is taken of both external and internal diffusion). Such knowledge provides a basis for design of the most efficient contactor system.

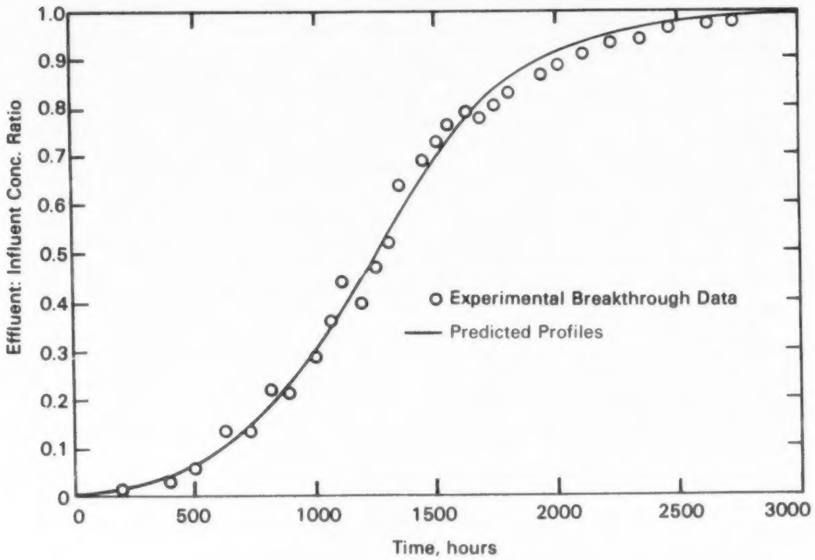


Figure 6. Concentration-time profile for a flow rate of 2 gpm/sq ft (81.4 1/min/sq m) in a 250-g fluid bed of 0.7111-mm carbon. Sorbate is dinitro-o-secbutylphenol (DNOSBP)[22]

Another form of mathematical modeling was proposed by Dostal, et al.[23] to obtain the best process control strategy and the design to achieve it. With only limited information concerning sorption equilibrium and rate, their model predicted the seasonal demand, i.e. the amount of GAC required as a function of time of year, given knowledge of the seasonal pattern of taste and odor encountered. The model also predicted the required rate of GAC regeneration which determined the size of regeneration system required. Estimates of process costs, while possible, were of limited use in the absence of reliable information on how taste and odor causing compounds are removed by GAC.

More complete descriptions of adsorption process dynamics presented in the 1970's covered the effects of contaminants competing for sorption sites, time dependent inlet concentrations and, simultaneous microbial degradation on the sorbent surface. These will be discussed later in more detail.

Factors Influencing Adsorbability

The most common way of describing adsorption of specific contaminants is by measuring the equilibrium distribution between the solid (adsorbent) and liquid (aqueous) phases. This distribution, or partitioning, is most often referred to as the adsorption isotherm, to acknowledge the fact that equilibrium adsorption is temperature dependent, increasing with decreasing temperature. Many such isotherms were developed in the 1960's for the alkylbenzene-sulfonates[14] (the essential component of detergents) and the organic pesticides[15]. These early isotherms were the forerunners for many more which were prepared in the 1970's as the catalog of organic contaminants continued to grow.

In its study of adsorption technology, which was supported by contract with the EPA, a subcommittee of the Safe Drinking Water Committee of the National Academy of Sciences (NAS) emphasized the wide range of adsorbabilities which have been measured[24]. As is shown in Fig. 7, the higher the surface (adsorbent phase) concentration, the better adsorbed is a given contaminant. It is also apparent that some of the notable halogenated aliphatic, trace contaminants of concern such as chloroform, bromodichloromethane, carbon tetrachloride, and trichloroethylene are poorly adsorbed in comparison to the aromatics, such as 2,4,6 trichlorophenol, which are more typical of pesticide derivatives. The widespread use of gas chromatographic analysis in the 1970's did much to expand the library of adsorption isotherms and to extend adsorption data down to the very low concentration of interest, i.e. 10^{-6} to 10^{-9} moles per liter (see Fig. 7). The lack of adsorption data in the low concentration range for most organic pollutants, however, was still of concern to EPA when it published the 1978 guideline report on GAC treatment[25].

Measuring the adsorbability of potential chemical carcinogens was a high priority of the 1970's. Adsorption tests, however, could be conducted only at the relatively few laboratories which were equipped to store and handle chemical carcinogens. A large fraction of such adsorption data was collected in an EPA-sponsored project at the Illinois Institute of Technology Research Institute[26]. Although there were exceptions, most compounds were found to be adsorbable, even at very low concentrations. The extent of adsorption, however, was quite variable, as might be expected from the large differences in physical and chemical properties among various classes of carcinogens; this variability is illustrated by the data presented in Table 4.

With most of the emphasis placed on data collection, there was a lag in sorting out general rules which could account for the many physical and chemical factors affecting adsorbability. As the list of organic contaminants grew, it was apparent that a predictive capability derived from such general rules could be of very practical use. The recent contributions by McGuire and Suffet[27], Manes[28], Belfort[29] and Weber and van Vliet[30], are quite significant in this respect. Their work returned attention to the fundamental physical and chemical principles which govern the interactions between the adsorbent and the contaminant, the adsorbent and water, and the contaminant and water.

The approach taken by McGuire and Suffet[27] derives from the principles of liquid-solid chromatography and provides for calculation of a thermodynamically based term referred to as net adsorption energy. This term is obtained from the solubility parameter which accounts for interactions among adsorbent, contaminant and water. The intent is to calculate the energy associated with transferring the contaminant from the polar solvent, water, to what is described as the non-polar surface of activated carbon; there is, however, considerable debate as to the importance of polar functional groups on GAC[30]. Aqueous solubility (which depends upon hydrogen bonding) and refractive index (which depends upon non-polar dispersive forces) are both important.

To test the net adsorption energy concept, McGuire and Suffet plotted experimental adsorption equilibrium data for 13 contaminants against their corresponding calculated net adsorption energies (Fig. 8). These results were encouraging in that a positive correlation seemed to emerge upon which the adsorption of other contaminants could be based. The distribution of calculated net adsorption energies for over 70 compounds identified in the Philadelphia raw water supply[31] is shown in Fig. 9. Highest energies were associated with the aromatics, e.g. substituted phenols and the lowest with the low molecular weight, chlorinated aliphatics, e.g. chloroform. If the concept put forth by McGuire and Suffet holds, the expected adsorbability of these organic compounds should range rather widely. Acceptance of this concept, however, must await further testing.

A group of researchers led by Manes[28] revived the very old concept proposed originally by Polanyi to explain the adsorption of gases. Known as the adsorption

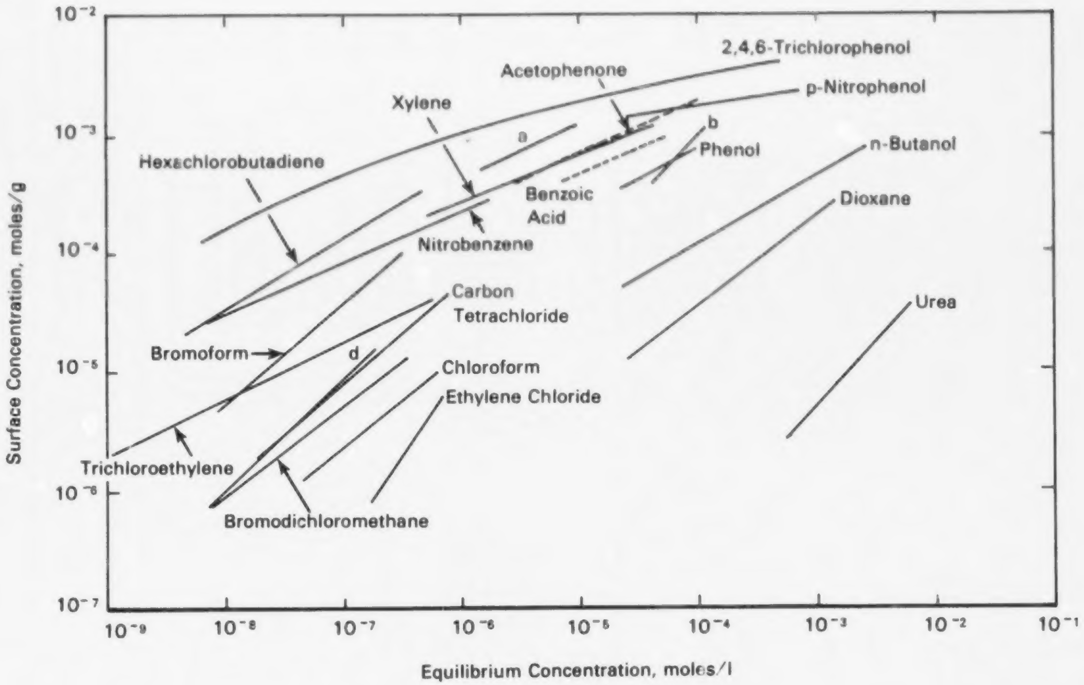


Figure 7. Specific adsorption isotherms. a-(di)-n-butyl phthalate; b-bis (2-chloroethyl) ether; c-dimethyl phthalate; d-dibromochloromethane[24].

Table 4. Summary of Carbon Adsorption Capacities Measured for Suspected Chemical Carcinogens[26]

Compound	Adsorption* Capacity, mg/g	Compound	Adsorption* Capacity, mg/g
bis(2-Ethylhexyl) phthalate	11,300	Phenanthrene	215
Butylbenzyl phthalate	1,520	Dimethylphenylcarbinol*	210
Heptachlor	1,220	4-Aminobiphenyl	200
Heptachlor epoxide	1,038	beta-Naphthol*	200
Endosulfan sulfate	686	alpha-Endosulfan	194
Endrin	666	Acenaphthene	190
Fluoranthene	664	4,4'Methylene-bis-(2-chlroroaniline)	190
Aldrin	651	Benzo(k)fluoranthene	181
PCB-1232	630	Acridine orange*	180
beta-Endosulfan	615	alpha-Naphthol	180
Dieldrin	606	4,6-Dinitro-o-cresol	169
Hexachlorobenzene	450	alpha-Naphthylamine	160
Anthracene	376	2,4-Dichlorophenol	157
4-Nitrobiphenyl	370	1,2,4-Trichlorobenzene	157
Fluorene	330	2,4,6-Trichlorophenol	155
DDT	322	beta-Naphthylamine	150
2-Acetylaminofluorene	318	Pentachlorophenol	150
alpha-BHC	303	2,4-Dinitrotoluene	146
Anethole*	300	2,6-Dinitrotoluene	145
3,3-Dichlorobenzidine	300	p-Nitroaniline*	140
2-Chloronaphthalene	280	1,1-Diphenylhydrazine	135
Phenylmercuric acetate	270	Naphthalene	132
Hexachlorobutadiene	258	1-Chloro-2-nitrobenzene	130
gamma-BHC (lindane)	256	1,2-Dichlorobenzene	129
p-Nonylphenol	250	p-Chlorometacresol	124
4-Dimethylaminoazobenzene	249	1,4-Dichlorobenzene	121
Chlordane	245	Benzothiazole*	120
PCB-1221	242	Diphenylamine	120
DDE	232	Guanine*	120
Acridine yellow*	230	Styrene	120
Benzidine dihydrochloride	220	1,3-Dichlorobenzene	118
beta-BHC	220	Acenaphthylene	115
N-Butylphthalate	220	4-Chlorophenyl phenyl ether	111
N-Nitrosodiphenylamine	220	Diethyl phthalate	110

*Adsorption capacities when equilibrium fluid phase concentration is 1 mg/L.

potential theory, it assumes a force of attraction to the adsorbent phase which is inversely proportional to the available unfilled adsorption space. The model considers only London forces of attraction, which are physical in nature. As such, it does not consider the interaction between sorbate, i.e. the contaminant being adsorbed, and specific functional groups on the adsorbent surface; this interaction is referred to as chemi-sorption. In reviving the Polanyi adsorption potential theory, then, Manes rekindled the great debate over the importance of physical adsorption forces vis a' vis chemical interactions with the surface[32].

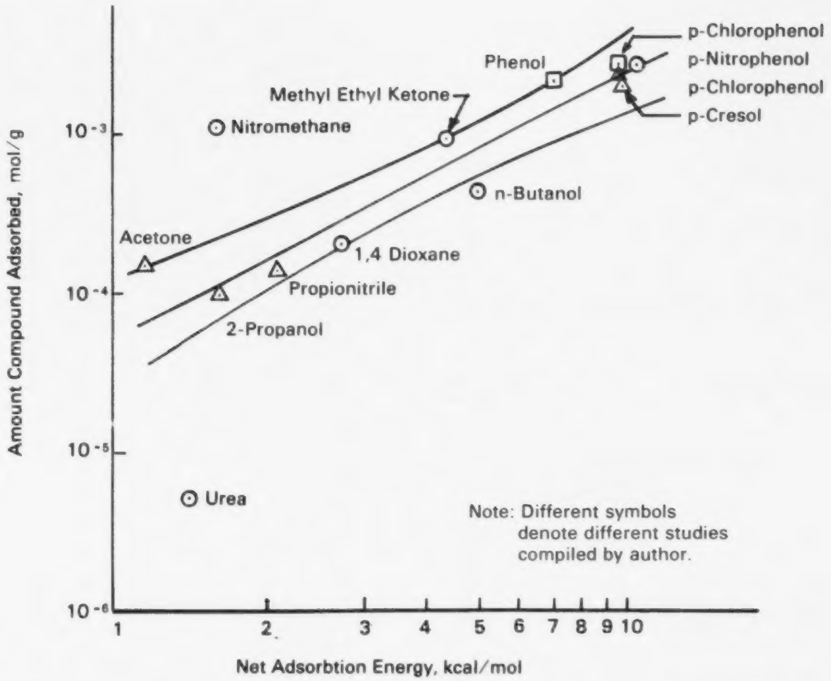


Figure 8. Relationship between the amount of compound adsorbed by activated carbon (at an equilibrium concentration of 10^{-3} mol/L) and the net adsorption energy[27].

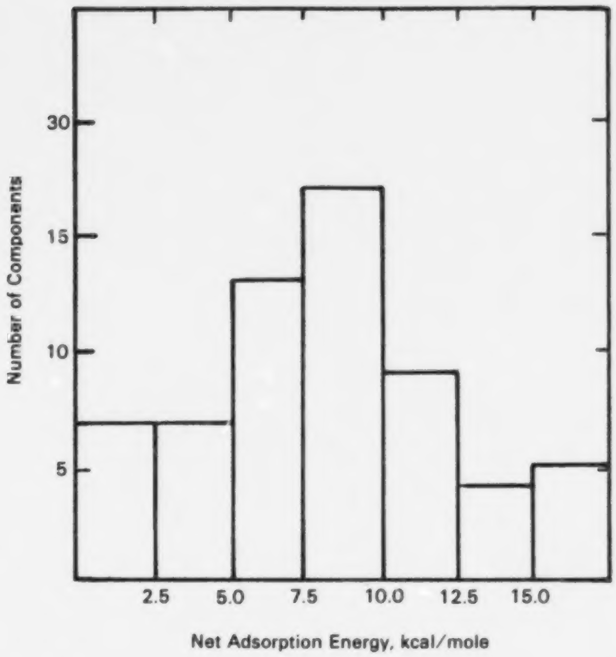


Figure 9. Distribution of net adsorption energy calculated for organic compounds identified in Philadelphia's water supply source. Such a wide distribution seems reasonable based on the wide range of organic compounds present. Highest energies were associated with aromatic compounds and lowest with low molecular weight, halogenated aliphatics(After McGuire)[31].

To adapt the theory for describing adsorption from the aqueous as opposed to gaseous phases, Manes took account of solubility (which replaces vapor pressure in the Polanyi model), molar volume (already included by Polanyi) and refractive index (a measure related to polarizability of the sorbate). This last factor represents the truly original contribution of Manes to the theory. Together, these three factors can be used to "scale" the adsorbability of any given contaminant (on a specific adsorbent) once the adsorption isotherm of just one reference sorbate is measured. Put in other words, it should be theoretically possible to "collapse" adsorption isotherms of different sorbates into one single "characteristic curve" by adjusting for the three scale factors.

The modified Polanyi model is similar in some respects to the net adsorption energy concept applied by McGuire and Suffet in that solubility and refractive index are included. However, the modified Polanyi model describes the entire shape of the adsorption isotherm, not just a single adsorption point. Its drawback is that calculations become highly involved when the sorbate is readily miscible in water and solubility no longer influences adsorption. An attempt was made to make practical use of the model in predicting adsorbability of trace organic contaminants in EPA-sponsored pilot plant studies at the Preston Water Treatment Plant in Hialeah (Greater Miami), Florida, hereafter referred to as the Miami, Florida Water Treatment Plant[33]. In this study, however, it was shown that the observed sorptive capacity for each of five volatile, chlorinated organic compounds was much less than predicted from the Polanyi model. Both competitive adsorption and errors in the Polanyi predictions were likely to have caused the noted discrepancies.

Belfort[29] has taken still another thermodynamic approach to predicting adsorbability which in this case derives from the field of reverse phase chromatography. The basis for his approach is the solvophobic theory which is used to describe the effect of the solvent (water) on the association reaction between the solute and the sorbent. This theory assumes the formation of a cavity in the solvent in order to accommodate the solute and the interaction of the solute with the solvent and the sorbent. In work sponsored by the EPA, he has explained how the theory may be simplified to allow its practical application. Using adsorption equilibrium data available from the literature, Belfort was able to use the theory to show the importance of both polar (caused by hydrogen bonding) and steric (caused by structural branching of the sorbate molecule) effects. Most interesting is his attempt to correlate adsorbability with just one factor, molecular surface area[34]. Molecular surface area relates to the free energy associated with the formation of a "cavity" adjacent to the sorbent surface. As is shown in Fig. 10, Belfort achieved reasonable correlations between amount adsorbed (Q_m) and the hydrocarbonaceous surface area (HSA) for several families of polar organic contaminants, e.g. acids, alcohols, aldehydes and ketones.

Most recently, Weber and van Vliet[30] took another approach which also draws upon the adsorption potential theory but in a different way than that described by Manes. In their research, the adsorption potential theory permits both the adsorbent and adsorbate characteristics to be examined quantitatively. Manes had been interested only in the latter.

Using molecular polarity of the test organic compounds as a comparative parameter, Weber and van Vliet were able to show that specificity of sorption sites was important for activated carbons but not for polymeric resin adsorbents. A much stronger adsorbent-adsorbate affinity is therefore produced in activated carbon adsorption. This is especially important in the very low concentration range of interest in water treatment where low solid phase loadings suggest intimate surface interactions. This affinity makes activated carbon a better adsorbent than polymeric resins; however, so-called carbonaceous resins (to be discussed later) were shown to have sorption affinities somewhat similar to activated carbon.

PROCESS DEVELOPMENT

The Case of THM's and Humic Substances

Much attention was given in the 1970's to the removal of low molecular weight, halogenated, aliphatic compounds such as members of the trihalomethane (THM) family, carbon tetrachloride, dichloroethane, tri- and tetrachloroethylene, and vinyl chloride. Pilot plant studies showed that many of these compounds began breaking through GAC beds after only one to two months of operation: illustrative breakthrough curves of chloroform at Philadelphia, Pennsylvania[35], total THM's at Cincinnati[25] and dichloroethane at Jefferson Parish, Louisiana[36] are given in Figs. 11-13, respectively. In removal of these contaminants, the service times are very short in comparison to those experienced when removing taste and odor or pesticides. This result might be predicted by examining adsorption equilibrium capacities given in Fig. 7.

Practical considerations limit the size of GAC contactors and thus, the empty bed contact time. Normally, replacement of a filter media with GAC gives the minimum acceptable EBCT of about five minutes. Construction of post filter adsorbers implies extension of EBCT to perhaps 20 to 25 minutes (with two beds in series). EPA pilot plant studies in Miami, Florida[33] provided experimental evidence of the sorption principle which states that longer service times are obtained as EBCT is increased (Fig. 14). In this figure service time is defined as the time for the concentration of

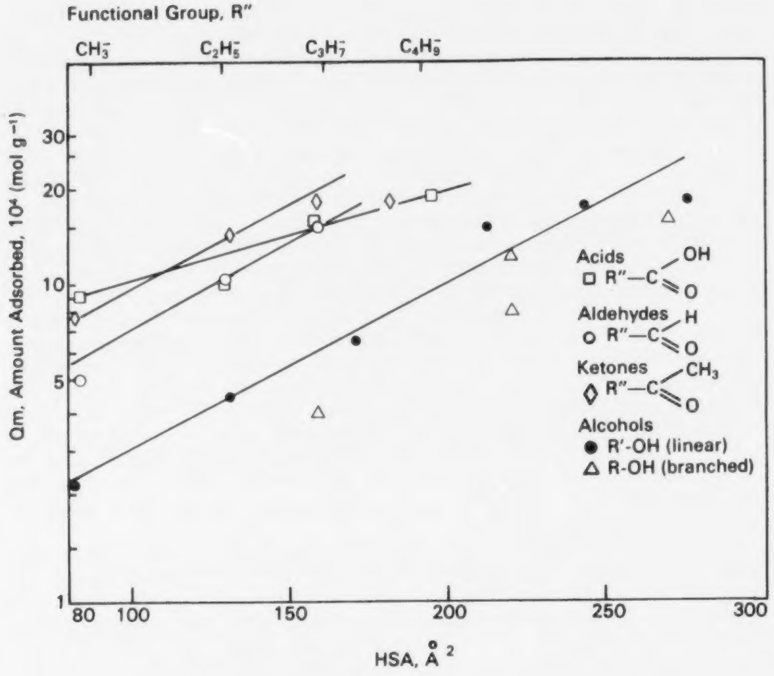


Figure 10. Plot of the logarithm of the extent of adsorption versus hydrocarbonaceous surface area for aliphatic alcohols, ketones, aldehydes, and acids as per the simplified solvophobic model[34].

each THM in the GAC bed effluent to reach 0.5 μg/L. Extending the EBCT from five minutes to 25 minutes provides a service time that is still less than three months in the case of chloroform removal. A longer service time would be the case if the full adsorption capacity of the bed were to be used. Regardless of the definition of service time employed, a much greater frequency of regeneration would be required for THM removal than for removal of taste and odors or pesticides. These findings prompted research on the effectiveness of alternative adsorbents, including synthetic resin materials; these will be discussed later.

Humic substances are naturally occurring, amorphous, macromolecules ranging in molecular weight from a few thousand to greater than 100,000. Their exact identity is still a matter of some speculation although certain functional groups are very well known. It is now well established that these humic substances react with chlorine to produce THM's and other chlorinated compounds. Therefore, one obvious function of adsorption would be to remove them before chlorination.

Because humic substances are formed in nature, they reflect the organic matter indigenous to a given location. Therefore, differences in their composition, reactivity with chlorine, and adsorbability can be expected. This was shown in EPA-sponsored work of McCreary and Snoeyink[37]. Wide differences in the adsorbability of a commercially supplied humic, fulvic acid extracted from leaves, and fulvic and humic acid fractions extracted from soils were apparent (Fig. 15). In each case, total organic carbon (TOC) was used as the surrogate parameter to measure the humic substances. Upon chlorination, these humic substances also produced different amounts of

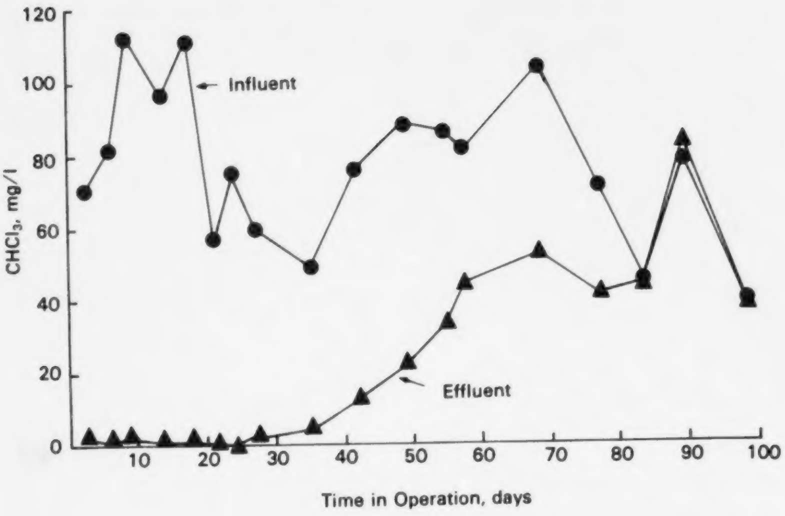


Figure 11. Chloroform breakthrough curve for filter-adsorber with EBCT = 15 min. at Philadelphia[35].

chloroform. Another interesting finding was the variability in adsorption of the various molecular weight fractions derived from a soil fulvic acid (Fig. 16). The larger molecular weight fractions were clearly less easily adsorbed (as measured by adsorption of TOC associated with each fraction). This was explained as being due to either molecular exclusion from pores or limitations in adsorption rate which prevented attainment of equilibrium in the time allotted. The results of research on adsorption of large molecular weight substances suggested the importance of pore size distribution of the adsorbent. This was proven nicely in follow-up studies by Lee and Snoeyink[38] and Lee, et al.[39]. Activated carbons varying widely in pore volume and pore size distribution were used to adsorb different molecular weight fractions of humic substances (Fig. 17). The results confirmed that assumption that adsorbability increased linearly with the pore volume contained in selected pore size ranges. Adsorption of the larger molecular weight fractions of the humic substances was related specifically to pores 100 to 500 Å in size, whereas adsorption of the smallest fraction was related to the micropores (less than 70 Å in size).

Lee and Snoeyink[38] also stressed the importance of coagulation as a pretreatment for GAC where humic substances are to be adsorbed: with such pretreatment, they noted an increase of fivefold in adsorption capacity and an increase in adsorption rate. Removal by coagulation of some poorly adsorbed fractions is only partly responsible for this improvement; there is also an adsorptive interaction between aluminum ions, used as the coagulant, and the humic substances. This conclusion was reached independently by Weber, et al.[40] and by Randkte and Jepsen[41]. Weber, et al. suggested the formation of an ion-humate-carbon complex. The impact of inorganic ions on the removal of a humic acid by GAC was illustrated vividly by comparison of the breakthrough curves obtained when tap water was used instead of distilled deionized water to prepare the feed solutions (Fig. 18). The tap water solution, which contained significant amounts of Ca, Mg, Fe, and OCl^-, produced much better removal of the humic acid. Weber, et al.[42,43] also showed that the adsorption of some organic molecules, such as the PCB's and dieldrin, may be enhanced by association with humic substances.

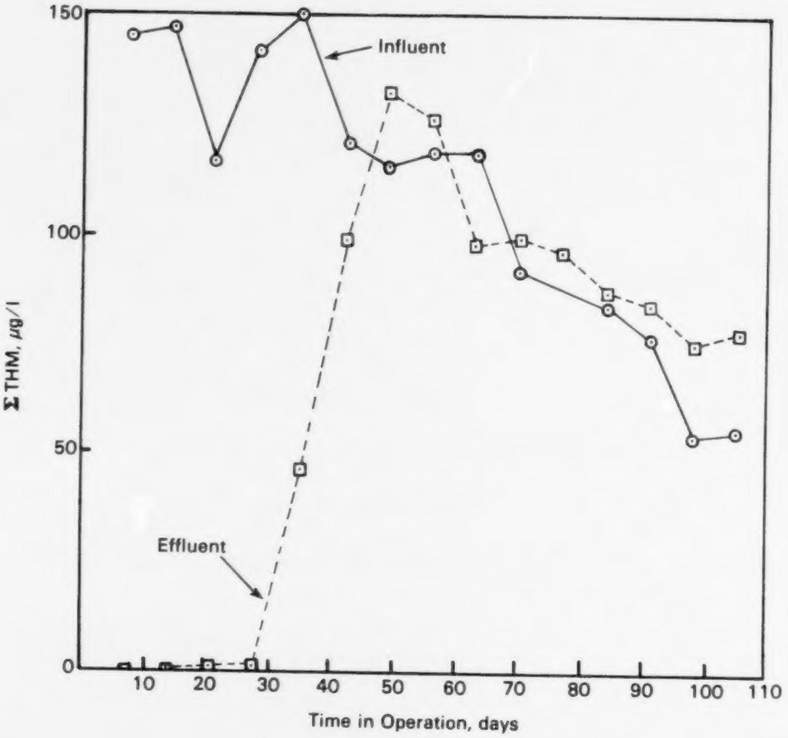


Figure 12. Total THM breakthrough curve with EBCT = 10 min. at Cincinnati[25].

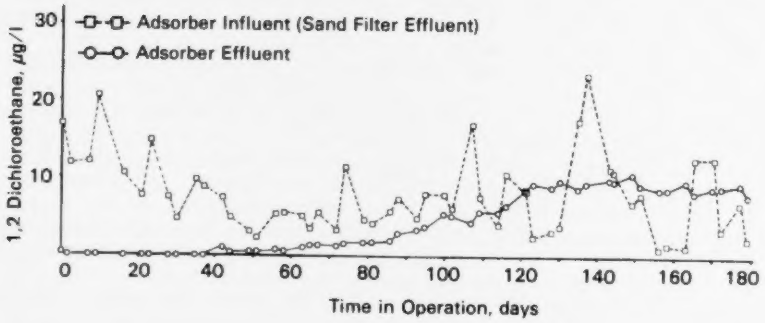


Figure 13. 1,2 DCE breakthrough curve for post filter adsorber (EBCT = 20 min) at Jefferson Parish, LA[36].

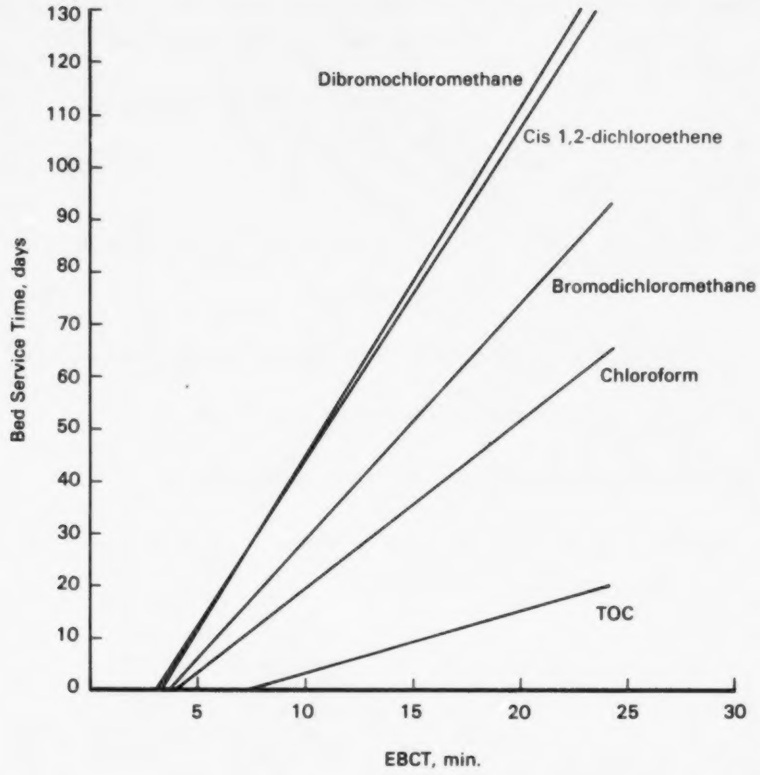


Figure 14. Relationship between bed service time and EBCT for several poorly adsorbed specific compounds and for background TOC[33].

Lee, et al.[39] have been successful in formulating and verifying a mathematical model of breakthrough. Their studies revealed that the diffusion of humic substances within the carbon's internal surface is very slow in comparison to other contaminants of concern; a similar result was reported by Weber, et al.[42]. This is undoubtedly due to the macromolecular character of these substances.

Because the type of activated carbon is so important in estimating sorptive capacity of humic substances (Fig. 17), it should also greatly influence the GAC service time. This was illustrated in the model predictions of Lee et al.[39] (Fig. 19a). Pretreatment by chemical coagulation has practical implications as is very well illustrated by comparing the breakthrough curves predicted by Lee, et al. before (Fig. 19a) and after coagulation (Fig. 19b). The time scale over which complete breakthrough occurs with pretreatment is an order magnitude longer (80 days) than without pretreatment (ten days).

One practical measure of the removal effectiveness of humic substances by GAC is the reduction in trihalomethane formation potential (THMFP). The THMFP is calculated as the increase in trihalomethane (THM) concentration which occurs upon reacting chlorine with the water sample for a specified time (usually two to seven days). Because GAC is expected to adsorb the precursors to THM, a reduction in

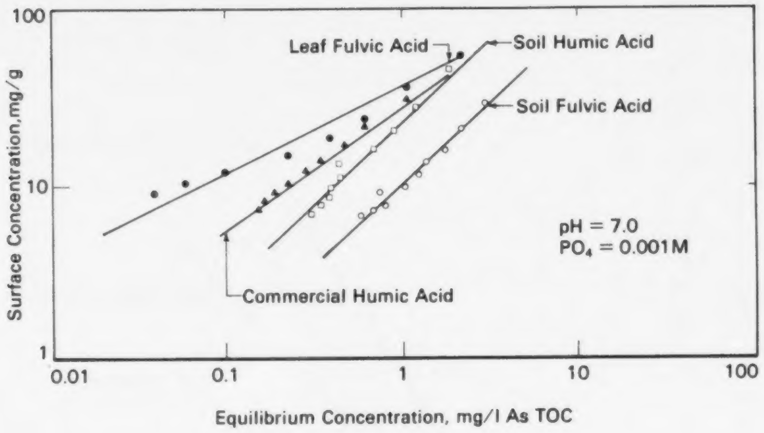


Figure 15. Adsorption of various types of humic substances[37].

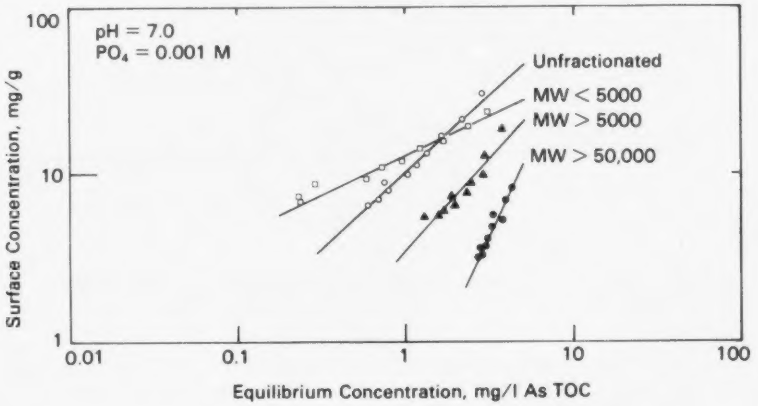


Figure 16. Adsorption of molecular weight fractions of soil fulvic acid[37].

THMFP should be measured when comparing influent and effluent of the GAC bed. This should also be qualitatively related to the removal of TOC across the GAC bed because TOC and THMFP generally reflect the presence of humic substances.

To show that mathematical predictions of breakthrough of humic substances, as measured by either TOC or THMFP, can in fact be quite useful, EPA pilot plant data from Jefferson Parish, Louisiana[36] on the breakthrough of THMFP was compared with results generated by Lee, et al.[39]. While the sources of the humic substances are of course completely different, the similarities in influent TOC, contact time and carbon type (actually the same) nevertheless justify the comparison. Fig. 20 shows that the THMFP rises steadily in the pilot plant study to a value of 100 μg/L after about 70 days. Lee, et al.[39] had correlated removal of TOC with reduction of THMFP in the laboratory and concluded that the value of 100 μg/L THMFP would

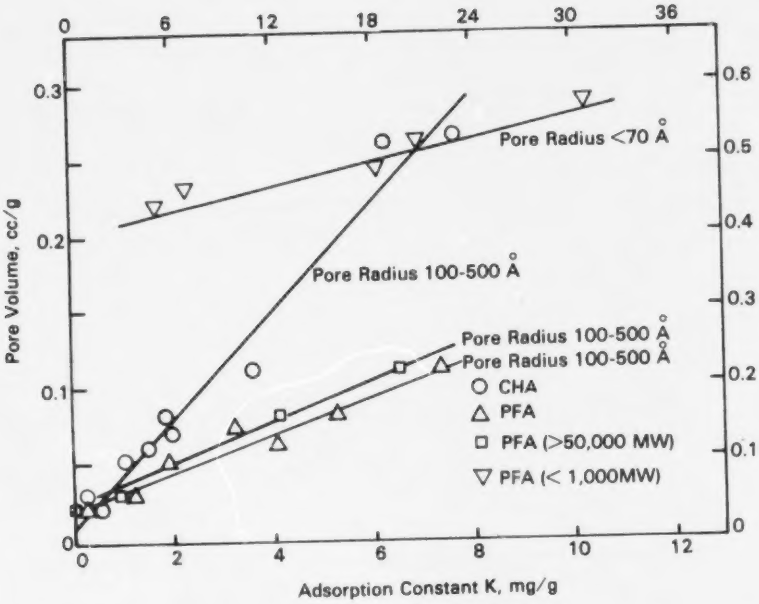


Figure 17. Adsorption constant of humic substances as a function of pore volume within a certain range of pore radii of carbon. Nine different carbon types were tested. CHA refers to commercial humic acid; PFA to peat fulvic acid; and PFA (250,000 MW) and PFA (<1000 MW) to specific molecular weight (MW) fractions of the peat fulvic acid[38].

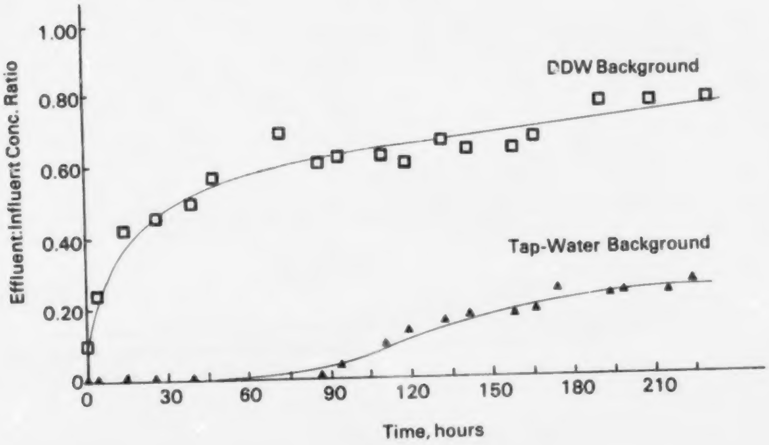
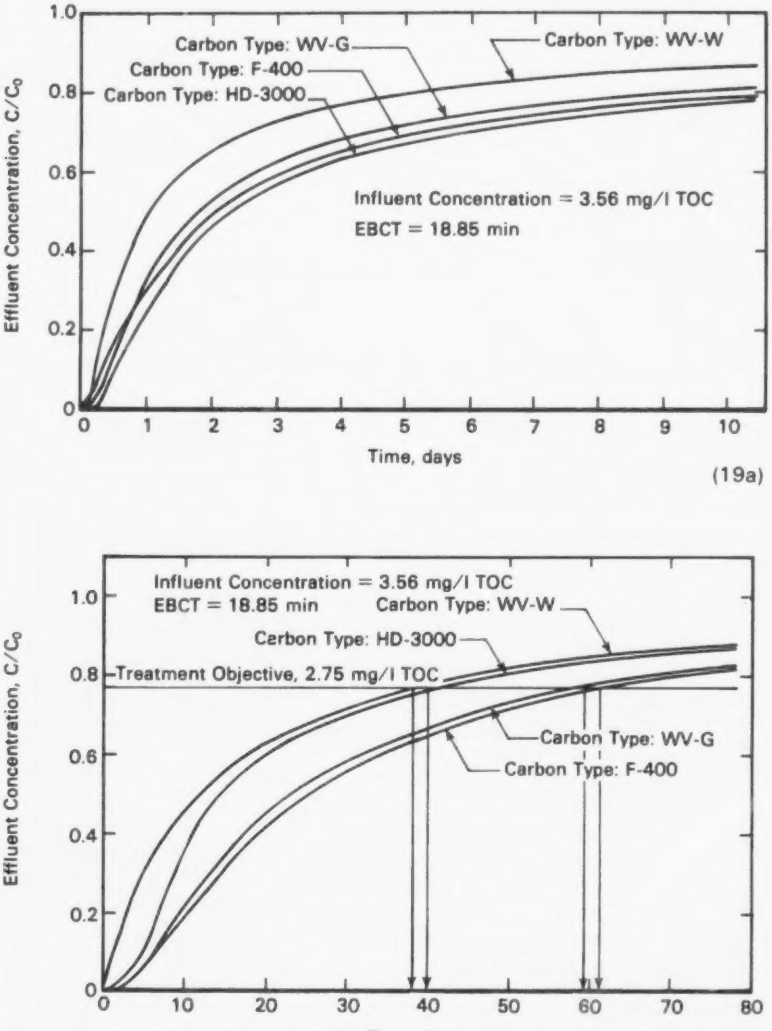


Figure 18. Effect of inorganic ions present in tap-water on the breakthrough profile for humic acids in granular carbon adsorption columns. DDW refers to distilled, de-ionized water[40].



(19a)

(19b)

Figure 19a and 19b. Model predictions of breakthrough curves for peat fulvic acid on different brands of activated carbon (a) before, and (b) after alum coagulation. Extent of TOC removal is shown normalized to influent TOC[38].

be reached when effluent TOC was 2.75 mg/L, or in about 60 days (see Fig. 19b). This is remarkably close to the time to reach 100 μg/L THMFP actually observed at Jefferson Parish.

An interesting feature of the breakthrough curve for terminal TTHM in Fig. 20 is the attainment of a plateau value which is significantly less than the influent value.

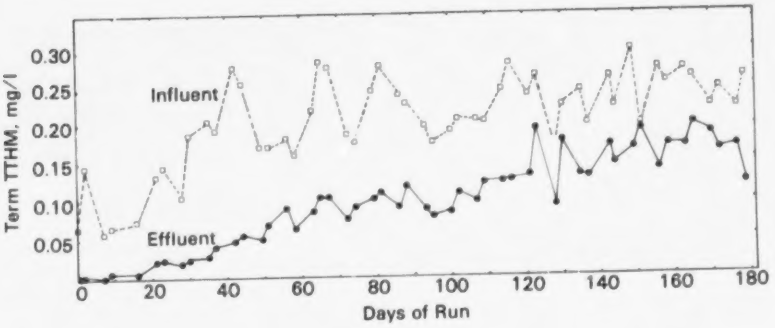


Figure 20. Performance of terminal TTHM through post filter adsorber (EBCT = 24 min) at Jefferson Parish, LA[36].

This has also been observed in other studies and explained as being due to biodegradation of humic substances. Weber,[40,43] in EPA-sponsored research, showed that biological activity must be considered for accuracy in predictions of humic substance breakthrough. Microbial degradation on adsorbent surfaces will be explored in more detail later.

Competition for Adsorption Sites

Competition for adsorption sites occurs when two or more contaminants are present in the feed to the GAC bed. The consequences of this phenomenon are that (1) sorptive capacity for each component is less than expected in the absence of competition, and (2) concentrations of some contaminants may actually be higher after GAC treatment than before. Sorting out of these effects has been a very difficult problem when analyzing the performance of pilot plants. This is understandable because raw waters contain so many different components in highly variable concentrations. Nevertheless, there was substantial progress in the 1970's in developing a better concept of how competition occurs in less complex mixtures.

The phenomenon of competitive displacement will be discussed for the case of a two-component system. The more poorly adsorbed component of the two exhausts sorption sites more rapidly and thus its breakthrough is expected first. As the active sorption zone advances down the bed, a region develops in which dynamic re-equilibration is occurring between the two components. Competitive equilibrium leads to displacement of some molecules of the more poorly adsorbed component which, as the adsorption zone finally exits the bed, manifests itself as a rise in effluent concentration temporarily above that of the influent.

There were numerous studies of two, and three component competition in GAC beds throughout the 1970's. An example is given in Figs. 21a and 21b for the case of p-nitrophenol -p-chlorophenol mixture[44]. It can be seen that as bed length (z), and thus contact time, increases, displacement of the more poorly adsorbed p-chlorophenol causes higher peak concentrations and a broadening of the band in which effluent exceeds influent concentration. The data show that while increasing contact time lengthens the service time of the bed, it also accentuates the effect of competition. The displacement effect may not be as noticeable in mixtures containing components differing widely in diffusivities. It may also be dampened when more than two components are competing.

Obviously, it would be counter-productive if the effluent of a GAC bed contained higher concentrations than the influent, particularly when maximum contaminant

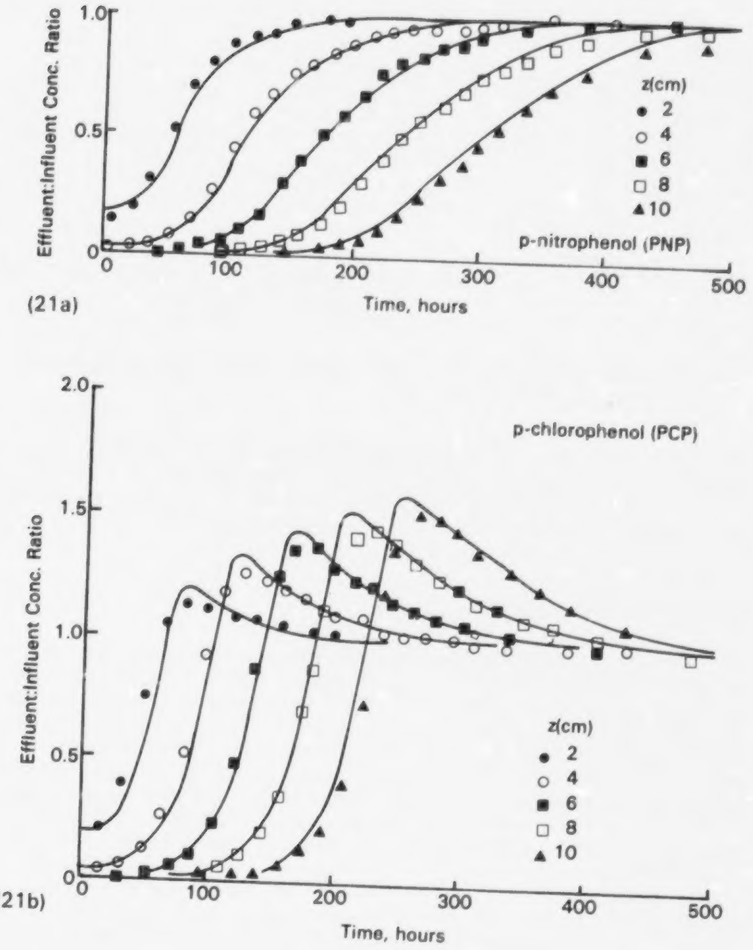


Figure 21a and 21b. Calculated (solid lines) and experimental (data points) breakthrough curves for PNP and PCP, respectively, in the PNP/PCP system at different bed depths. Mass transfer controlled by film diffusion and competitive equilibria described by the IAS model[44].

levels may be enforced. However, there have been very few pilot plant studies where the displacement effect could be observed. The most notable cases have involved the poorly adsorbed THM's and other low molecular weight, chlorinated hydrocarbons such as vinyl chloride[25]. But even in these instances, a sudden decrease in influent concentration could have produced the same effluent concentration pattern. Drawing the distinction between the effects of fluctuating influent concentration and competitive adsorption is a common problem in interpreting pilot plant results.

Another manifestation of competition is the domination of adsorption sites by just one component. For example, Suffet, et al.[45] reported that an accidental spill of toluene in the Philadelphia raw water supply resulted in no adsorption of 30 other contaminants present in much lower concentrations. Following the spill event, these compounds here again adsorbed; still later, changing feed concentrations of various components caused another re-equilibration and it was accompanied by desorption of several components, including toluene.

The overwhelming portion of organic matter is composed of humic substances which might compete with trace contaminants for adsorption sites. One interesting example of competition is that between humic substances and odor causing compounds. The early work of Rosen, et al.[46] at the EPA identified specific organic compounds which were responsible for odors, namely methylisoborneol (MIB), a metabolite of actinomycetes, and geosmin, a metabolite of actinomycetes and blue green algae. Herzing, et al.[47] showed how these two compounds, when present in trace amounts, are adsorbed in competition with much higher concentration of humic substances. Although some competition did occur, the typical displacement effect was not observed. In fact, once MIB was adsorbed, it was very difficult to desorb. These observations helped to explain why GAC beds have been so successful in removing taste and odor causing compounds which are well adsorbed and present in such very low concentrations as to be relatively unaffected by competition.

Competitive adsorption of carbon tetrachloride, which is poorly adsorbed, and humic substances provides a contrasting example. In EPA studies, Weber et al.[43] examined the breakthrough curve with and without competition. Carbon tetrachloride was first adsorbed from distilled water until complete breakthrough occurred (Fig. 22). Then, distilled water alone was fed resulting in significant desorption of carbon tetrachloride. Subsequent to the distilled water feed, a humic acid feed was introduced. This produced the expected rise in carbon tetrachloride concentration as a result of competitive displacement. In a similar experiment involving removal of the much more strongly adsorbed component, dieldrin (pesticide), Weber, et al.[43] observed little desorption or competitive adsorption in the presence of humic substances. The point here is that the energy of adsorption associated with the trace contaminant controls the extent to which displacement occurs. In the case of strongly adsorbed MIB and dieldrin, for example, competition may not be important.

It has already been discussed that adsorbability of humic substances depends upon their source. This characteristic applies to competitive adsorption with trace contaminants as well. Murin and Snoeyink[48] found notable differences in the extent of competition depending upon the source of humic substance. In the presence of each of these humic substances, adsorption of the trace contaminant, 2,4,6 trichlorophenol was reduced somewhat differently, but in general on the order of 50 percent due to competitive effects.

The research team at the University of Karlsruhe in Germany, led by Professor Sontheimer, has been seeking a practical way of evaluating competitive adsorption between background organic matter, i.e. humic substances, and trace contaminants. In their approach, they have found that flocculated lignin sulfonic acid simulates the sorptive behavior of the background organic matter and serves as a convenient model compound[49]. Competition with trace contaminants is simulated by addition of paranitrophenol. Mathematical modeling of equilibrium adsorption gives a practical method of comparing the effectiveness of different activated carbons under this test condition.

A reasonably solid foundation for understanding of competitive adsorption evolved in the 1970's with the aid of mathematical modeling. Research teams in the United States and Europe, working on this problem from different directions, seemed to reach some sense of agreement on the principles involved.

Mathematical models of competitive adsorption developed by different groups share a common framework. The need for a competitive equilibrium model is foremost in importance. The dynamic aspect of GAC bed operation further requires a

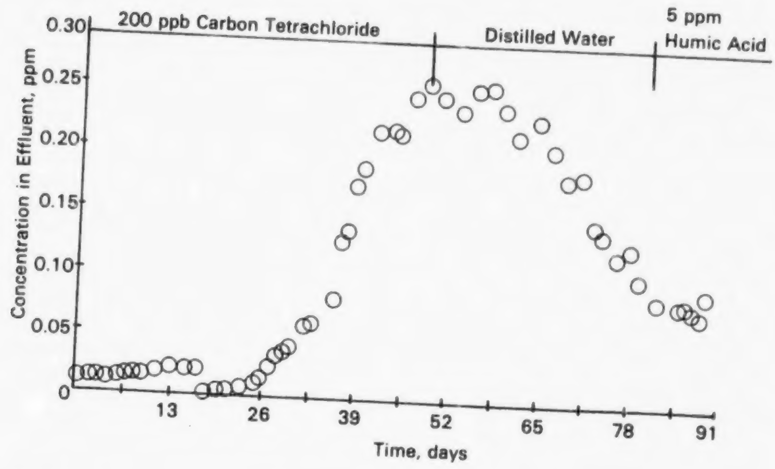


Figure 22. Experimental breakthrough, desorption, and displacement profiles for carbon tetrachloride[43].

description of diffusional transport of more than one component through the internal pore structure. This can be complicated, as has been well recognized by Crittenden and Weber[50] and by Fritz, et al.[44], especially if the components have widely different diffusion coefficients. Under such conditions, it is possible for the faster diffusing component to reach adsorption sites without encountering competition, only to be displaced later by the slower diffusing component. This sets up a complicated counter diffusion pattern within the pore structure until final equilibrium is achieved. Although different assumptions regarding the form of the competitive equilibrium relationship and the rate-limiting step of sorbate transport have been used, the breakthrough curves produced by various models are somewhat similar and resemble those given earlier in Fig. 21. However, assumptions regarding equilibrium and kinetics can be quite critical in obtaining agreement between experimental data and model predictions.

One of the most significant developments of the 1970's was the adaptation of the ideal adsorbed solution (IAS) theory to describe competitive equilibrium. This theory had originally been developed by Myers and Prausnitz[51] to predict the adsorption of gas mixtures and later adapted by Radke and Prausnitz[52] for use in dilute aqueous mixtures. Prior to this development the competitive Langmuir model was the most widely used but not always successfully[53-55].

The thermodynamic principle involved in the ideal adsorbed solution theory does not require an assumption that single solute adsorption must follow a prescribed model, or that each component must adsorb to the same extent when ultimate capacity is reached as is the case for the more commonly used Langmuir competitive model. Instead, the IAS theory applies to any equilibrium distribution measured experimentally in single solute systems. Such data can then be manipulated to calculate what is known as the spreading pressure function. Spreading pressure and surface area for the two-dimensional adsorbed phase are analogous to pressure and volume in a real fluid. This analogy is applicable also to describing competitive adsorption in that each component must exert a spreading pressure equal to that of the mixture. The rather involved thermodynamic arguments have been effectively presented by Radke and Prausnitz[52].

Several investigators have independently applied the IAS model. The best documentation is provided by, Fritz and Schluender[55], Jossens, et al.[56], and Singer and Yen[54]. Despite the success claimed and the advantages over the Langmuir model, there have been notable exceptions, too[50,55,56,57]. One problem that seems to persist is that components differing widely in molecular structure, such as 2,4 dichlorophenol and dodecylbenzenesulfonate, do not compete as expected. Crittenden and Weber[50] recognized this difficulty and decided not to adopt the IAS model for use in dynamic column performance predictions.

Assumptions regarding sorption kinetics are also important. Many of the early models considered the rate of transport of solutes to be limited by resistances offered by the external, laminar film surrounding the carbon particles and by internal pore diffusion. However, in the 1970's, there was evidence presented by several research teams[39,44,50] that surface, rather than pore diffusion was occurring in the sorbed phase itself. This concept seemed better able to account for the influence of feed concentrations. Nevertheless, at least two groups (Crittenden and Weber[50] and Fritz, et al.[44]) recognized that even this model could not explain the interactions observed for two components differing widely in diffusivity. In this case, the rate of adsorption of the faster diffusing component is slowed and that of the slower diffusing component accelerated. Only by adjusting diffusion coefficients artificially and somewhat arbitrarily was it possible to predict breakthrough.

The sorptive affinity of trace contaminants relative to the background humic substances can be very important in determining the service time of the bed. Wilde[58] adopted a dynamic, fixed-bed model of competitive adsorption to show this effect by computer simulations. In his work, TOC was taken as the indicator of humic substances and acceptable service time as the time for the effluent to reach one percent of the influent concentration of the trace contaminant. Fig. 23 shows quite logically that as the sorptive affinity of the trace contaminant increases relative to that of the TOC, i.e. as α increases, the service time increases. This is because the trace contaminant is able to compete much better with the TOC for sorption sites and is therefore adsorbed to a greater degree.

One other important competitive effect is that produced by variable component concentrations in the feed to the adsorbent bed. Weber and co-workers developed MADAM (Michigan Adsorption Design and Applications Model) to handle this as well as other problems of practical concern[50,59,60]. Another model developed by Balzli, et al.[61] was used specifically to examine the effect of a sudden increase in the influent concentration of one component on the time to the beginning of breakthrough of each component. Increasing the concentration of the less strongly adsorbed component accelerated its breakthrough, but delayed the beginning of breakthrough of the more strongly adsorbed component. Practical application, however, of models to predict the effect of discontinuities in influent concentrations to adsorption beds is very difficult because of the large number of competing components which would have to be considered. The recent work of Thacker, Snoeyink and Crittenden[62] shows that at least for two component systems, the displacement effect can be predicted quite well. Their results indicate, for example, that effluent THM will remain above the influent concentration for many weeks if the influent THM concentration is suddenly lowered.

Adsorption on Synthetic Resins

The relatively low sorptive capacities measured for low molecular weight, chlorinated compounds such as the THM's, carbon tetrachloride and trichloroethylene (see Fig. 7) were of considerable concern in the 1970's because these specific substances may be targeted for removal. The practical consequence of poor adsorbability is limited service times of GAC beds. This is well illustrated by the EPA-sponsored pilot plant studies at Miami, Florida[33], which showed that service time for several of these contaminants was less than 100 days, even at very long contact times (see Fig.

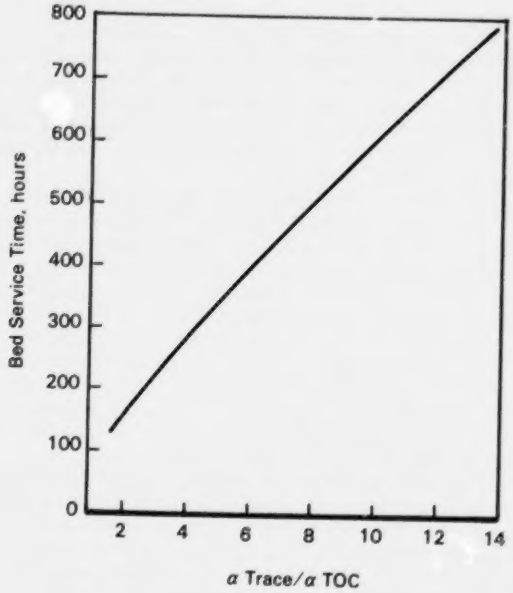


Figure 23. Bed service time vs ratio of trace to TOC background selectivities[58].

14). In addition, service time on the basis of TOC removal was also severely limited. TOC is largely a measure of humic substances and must be removed in order to prevent reaction with chlorine to form THM's.

Although activated carbon is an effective adsorbent for a broad spectrum of compounds, it is clear from several pilot plant studies that its performance capabilities can be unnecessarily underutilized if certain, poorly adsorbed contaminants must be removed. Alternative adsorbents, therefore, were sought in the 1970's. Synthetic resins were potentially attractive because design of resins with specific physical and chemical properties could make them more selective adsorbents than activated carbon. The possibility therefore existed that these resins could be used to complement the removal functions of activated carbon.

New resin materials did not fit the classical description of ion exchangers. Some have porous, polymeric matrices composed of either styrene-divinylbenzene (Rohm and Haas XAD-2) or an acrylic ester (Rohm and Haas XAD-8). Others developed more recently are designated as carbonized resins (Rohm and Haas XE 340, XE 347 and XE 348) and have chemical and physical characteristics approaching those of activated carbon.

Polymeric resins were first used to concentrate and recover organic contaminants for further chemical identification. Recovery is obtained by first adsorbing the contaminants on the resin and then desorbing them into an organic solvent. Weber and van Vliet[30], explained that polymeric resins should perform better than GAC for this purpose because such resins do not bind the sorbed compound as tightly as does activated carbon. This feature however, is not necessarily desirable when permanent removal of the contaminant is the objective nor does it indicate better adsorption properties.

A pilot plant study of XAD-2 and activated carbon adsorbents was conducted in Philadelphia. Sophisticated GC-mass spectroscopy monitored the removal of specific contaminants across XAD-2 and GAC adsorbent materials. These results, reported by Suffet, et al.[63], did not show the resin to be superior to GAC. Many compounds appeared much earlier in the effluent of resin than the GAC system; in addition, there was significant desorption of several other compounds.

The adsorption efficiency of carbonized resins for specific contaminants was a great improvement over that of the polymeric resins. These resins are characterized by less pore volume than activated carbon and with pore sizes in a much narrower range than activated carbons; in particular, there are few pores greater than 300 Å. Internal surface area is also much less than found in activated carbon (350 M^2/gm to 500 M^2/gm vs 650 M^2/gm to 1100 M^2/gm). The XE 340, XE 347 and XE 348 resins do differ in their pore size distributions; it is suggested that these differences provide an opportunity for matching the resin with the treatment objective. Another distinguishing feature of resins is the availability of adsorbents with different hydrophobicities. XE 340, for example, has a very non-polar, hydrophobic surface which favors adsorption of such compounds as the THM's.

An EPA pilot plant study[64] in Cincinnati showed that XE 340 resin was still removing THM's after 40 weeks (Fig. 24) whereas GAC was only effective for eight weeks (see Figs. 11 and 12). A more detailed pilot plant evaluation in Miami, Florida, indicated that in addition to the THM's, dichloroethenes, trichloroethylene, chlorobenzene and vinyl chloride were all more effectively removed by this resin[33]. The amounts adsorbed were about three times greater than that for GAC treatment. The advantage of resin adsorption was not as clearly shown, however, in other pilot plant studies at Kansas City, Missouri[65] which were sponsored jointly by the EPA and the American Water Works Association Research Foundation. While XE 340 was a better adsorbent for chloroform than most types of activated carbons evaluated, it was far less effective as an adsorbent for TOC.

Controlled laboratory experiments by Chudyk, et al.[66] explained how XE 340 could in some cases adsorb chloroform better than activated carbons. It was reasoned that the large volume of small pores favors the adsorption of chloroform while excluding humic substances. Activated carbons, on the other hand, can adsorb both because of the much wider range of pore sizes available. This produces competition which lowers the adsorption capacity with respect to chloroform. In the absence of competition by humic substances, it was shown in fact, that some activated carbons adsorb chloroform as well as do the resins.

One concept advanced was use of two different resin beds in series. The first would remove the THM precursors, i.e. the humic substances and the second, the low molecular weight, halogenated organic contaminants. European research had indicated that both strong and weak base ion exchange resins could remove humic substances. For example, both Kolle[67] in Germany and Rook[68] in the Netherlands reported success with strong base resins in pilot plant and full-scale studies. Later, Rook and Evans[69] switched to a more specific removal measurement, the THMFP test, and showed that weak base resins could also be used. They indicated the practical advantage of these resins in terms of chemical regeneration efficiency; service time, however, was still quite limited.

In studies sponsored jointly by the EPA and the American Water Works Association Research Foundation, Boening et al.[70] compared various resins for removal of humic substances. As Fig. 25 indicates, the best adsorbent was a strong base, macroporous resin. However, because of the difficulty in regenerating this resin, these researchers suggested use of a weak base resin instead although their results showed that an activated carbon having a pore-size distribution favoring larger pores would perform about as well as weak base resins. Pilot plant results as Kansas City, Missouri[65] and at Miami, Florida[33] generally supported the argument that strong base resins remove humic substances rather well. It was also apparent that some activated carbons performed equally well. Though not specifically discussed in the pilot plant reports, the carbons which performed the best were those having the most pore volume associated with the largest pores. This was reported independently in more carefully controlled, laboratory studies by Boening, et al.[70] and by Lee and Snoeyink[38].

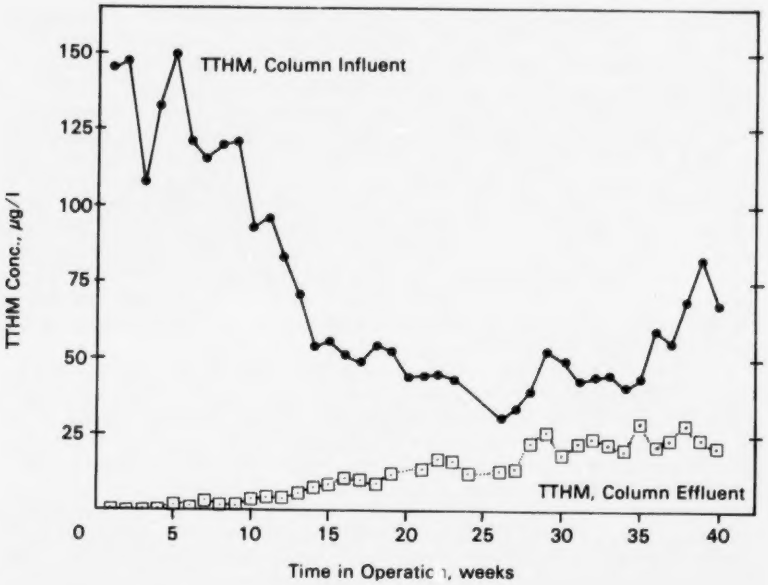


Figure 24. Removal of trihalomethanes by Ambersorb® XE-340 (EBCT = 10 min)[64].

The question of when and how to use synthetic resins is open to debate. Carbonaceous resins may provide a solution when a few, specific contaminants must be removed as might be the case in groundwater treatment. When humic substances are important, as is the case for many surface waters, then GAC seems to perform about as well as weak base resins. Much of the debate, however, centers about the economics and efficiency of synthetic resin regeneration.

Regeneration of Adsorbents

For adsorption to be economically feasible, the adsorbent must be regenerated several times. The initial investment in the adsorbent is very large. For example, the charge of GAC required to fill the contactors in a plant serving 75,000 people would be on the order of 500,000 pounds at a cost of about 60 cents per pound. With service time being from three to six months, it is obvious that the adsorbent cannot be used on a throw-away basis.

Regeneration consists of (1) transporting the spent adsorbent from the contactor to the regenerating facility; (2) removing sorbed organics from the sorbent structure using either thermal reactivation, or in the case of resins, organic solvents, steam, or brine; and (3) returning the reactivated adsorbent to the contactor. Efficient regeneration depends on minimizing the adsorbent losses during transport and regeneration, and restoring the virgin adsorbent properties, or nearly so. To be practical, energy costs must be reasonable and by-products, such as the sludge from slurry transport, must be easily handled.

Advances were made in regeneration technology in the 1970's, particularly for application in water treatment plants. The economic necessity of on-site regeneration was recognized in Germany[71] and Switzerland[72]. Several plants installed what is referred to as a fluidized-bed furnace. This new type of furnace has several advantages

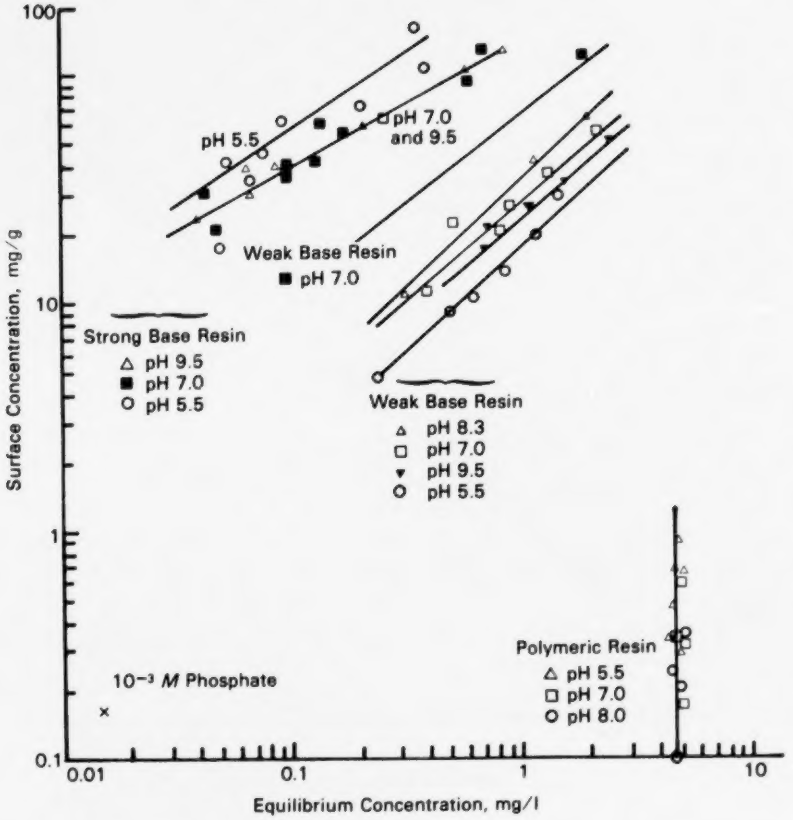


Figure 25. Commercial humic acid isotherms as a function of pH of weak base resins, strong base resin and polymeric resin[70].

over the multiple-hearth furnace, which was so well known in the United States as a result of advanced waste treatment research, e.g. at Lake Tahoe. In particular, the fluidized-bed furnace is far less complicated, more compact, provides more rapid heat and mass transfer and minimizes carbon losses due to abrasion.

European experience during the late 1970's was very encouraging. Results of equilibrium adsorption tests at the Wuppertal water works of Germany after one, three and five regeneration cycles are compared in Fig. 26 with those of fresh activated carbon[73]. In this plant, the practical parameter used to assess the effectiveness of regeneration is the amount of ultraviolet (UV) absorbing material (△ UV) which can be removed by the activated carbon when added to the raw water in various dosages. As seen, regeneration restored the carbon to its original effectiveness by this measure.

A dynamic rather than equilibrium test of effectiveness was adopted at Dusseldorf, Germany using measurements of the reduction in UV absorbing material across full-scale GAC beds[74]. An empirical, semi-logarithmic relationship was developed between the percent reduction in UV absorbance and the volume of water processed.

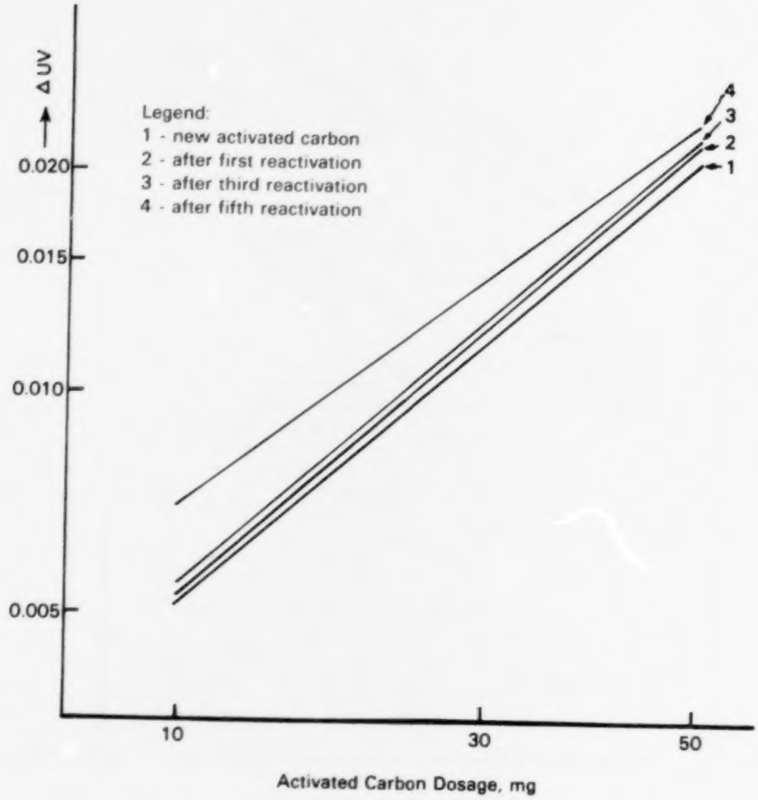


Figure 26. Adsorption isotherms after repeated regeneration.[73]

Fig. 27 is a typical result obtained for fresh and regenerated carbon, showing that there was little difference in the rate at which adsorption efficiency decreased with volume processed.

Although European data suggested that regeneration was effective, this issue had not been addressed in the United States with the exception of one short-lived project (employing a multiple-hearth furnace) at the Nitro, West Virginia facility. The need to demonstrate regeneration in the United States was also sharpened by the lack of information on effectiveness of GAC in removing specific contaminants after several cycles. In response, three demonstration projects were initiated by the EPA at Manchester, New Hampshire, Passaic Valley, New Jersey and Cincinnati, Ohio[75].

The fluidized bed is being used at Manchester and Cincinnati; the electric furnace is used at Passaic Valley. The fluidized bed has already been discussed. The electric furnace, a relatively new concept, utilizes infra-red energy for regeneration and is described as (1) providing an alternative to use of scarce fossil fuels, and (2) enabling start-up and shutdown without long warm-up and cool-down periods[25].

Only preliminary results are so far available from these United States projects and the bulk of the data is from operation of the electric furnace installation at Passaic Valley. Here, carbon has been regenerated successfully for two cycles[76]. In this case,

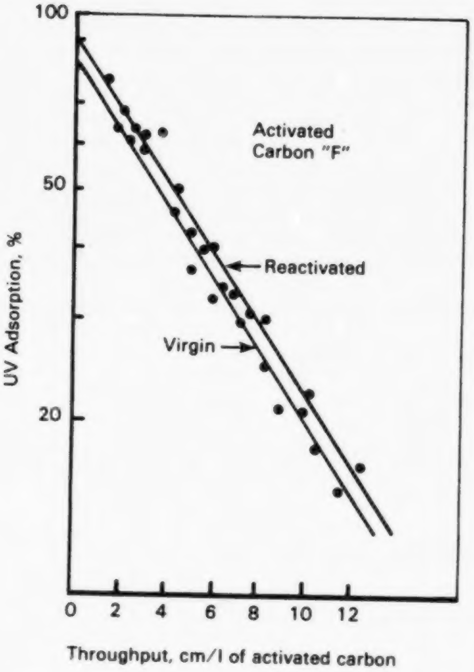


Figure 27. Dynamic testing of regeneration effectiveness in full-scale testing of GAC bed performance in Dusseldorf, West Germany[74].

success is defined in terms of the two traditional parameters used to characterize activated carbon: the iodine number (indicating pore volume and surface area) and apparent density (a reduction indicating removal of sorbed material), and by such recently adopted parameters as reduction in TOC and total organic halogens (TOX). Carbon losses were within acceptable limits, i.e. between 4 and 7 percent. Initial reports from the fluidized-bed facility at Manchester also indicate success[77]. However, carbon losses were about 11 percent and according to the traditional measures of adsorbent effectiveness, the carbon was restored to near its virgin state. At both Manchester and Passaic Valley, important problems were encountered with transport of carbon to and from the furnace; it is believed that as experience is gained these can be overcome.

Two other studies in the United States have involved evaluation of the effectiveness of regeneration, although they did not include on-site facilities. The EPA/American Water Works Association Research Foundation project at Kansas City, Missouri examined the ability of regenerated carbon to remove TOC and total trihalomethanes (TTHM)[65]. There was little difference in performance of fresh, once and twice regenerated carbons. Another interesting, although expected observation, was that simply steaming the GAC bed routinely would be sufficient if the purpose of regeneration was limited to restoration of TTHM removal capacity; in this case, steam volatizes the TTHM's.

Similar studies were conducted at the Philadelphia pilot water treatment plant[78]. However, here the emphasis was on the effect of the gasification temperature (the last stage of regeneration in which the carbonaceous residue is oxidized) on the restoration of virgin carbon properties. It had been feared that data derived from earlier regeneration experience with carbon in wastewater treatment might not be useful in selection of gasification temperature for regeneration of carbon used in water treatment. In wastewater applications, the loading of adsorbed organic contaminants is far greater and thus the required gasification temperature may be much higher. These water treatment studies indicated that the sorptive capability of GAC with respect to chloroform was in fact impaired if the conventional gasification temperature (1750° F) were used; a temperature of 1550° F gave better results. However, if regeneration effectiveness were measured by TOC adsorption rather than by chloroform adsorption, gasification temperature made little difference. It was suggested that selective destruction of micropore space by high temperature may affect adsorption of chloroform but not of humic substances, which comprise a significant fraction of TOC.

Experience with regeneration of synthetic resins is even more limited. Steam was used effectively to regenerate the carbonaceous resin, XE 340, in Kansas City pilot tests[65]. However, Chudyk, et al.[66] were not able to remove sorbed methylisoborneol, an odor-producing compound, with either steam or steam plus ethanol. Strong base resins proposed for removal of humic substances can be regenerated with mixtures of caustic and sodium chloride. Less caustic is required for weak base resins which must still be rinsed with hydrochloric acid. As Boening, et al.[70] point out, there are still many questions to be answered regarding regenerant selection and ultimate disposal of the waste brine.

Microbial Activity on Activated Carbon

An intriguing process explored in the 1970's was the combination of biodegradation and adsorption to achieve more efficient removal of organic contaminants in water treatment. A thorough review of research findings is provided in a recent Committee Report of the American Water Works Association[79]. Microbial growth is known to occur on sand grains; this was especially true for slow sand filters used widely to treat water at the turn of the century. However, the extent to which biodegradation by attached microbial growths may account for removal of trace organic contaminants in this process was largely unknown. In contrast to a non-adsorbent material such as sand, activated carbon affords the opportunity of "temporary storage" for substances which are rather difficult to biodegrade. By providing a longer time of contact between the microbial population and the substrates, such storage could promote microbial acclimation and subsequent biodegradation.

An interplay between the adsorption and biodegradation processes may exist. This could lead to *in situ* regeneration of sorption sites. Although it has not been rigorously proven, Sontheimer and his co-workers were first to suggest that *in situ* regeneration was occurring in pilot plant studies at the Bremen water works in Germany[80]. Several research groups followed up with mathematical descriptions of the interaction between biodegradation and adsorption[81-83]. According to most investigators, biodegradation increases in importance as the adsorption capacity becomes exhausted and substrate concentration begins to build in the fluid phase adjacent to the biofilm in the carbon particles.

The only substrate considered available in most models is that external to the particle. This interaction is depicted schematically in Fig. 28. Biodegradation begins in the uppermost portion of the bed which, in downflow operation, is first to become exhausted. As service time increases, the active adsorption zone moves down the bed. It is followed by the freshly exhausted zone which has yet to build up to maximum intensity of microbial activity, and then by the active biodegradation zone.

Conceptual mathematical models of this process were an outgrowth of adsorption models. Typical breakthrough curves, with and without biodegradation, are given in Fig. 29. Instead of effluent concentration approaching influent concentration as sorption capacity is depleted, a steady-state removal is attained across the bed due to

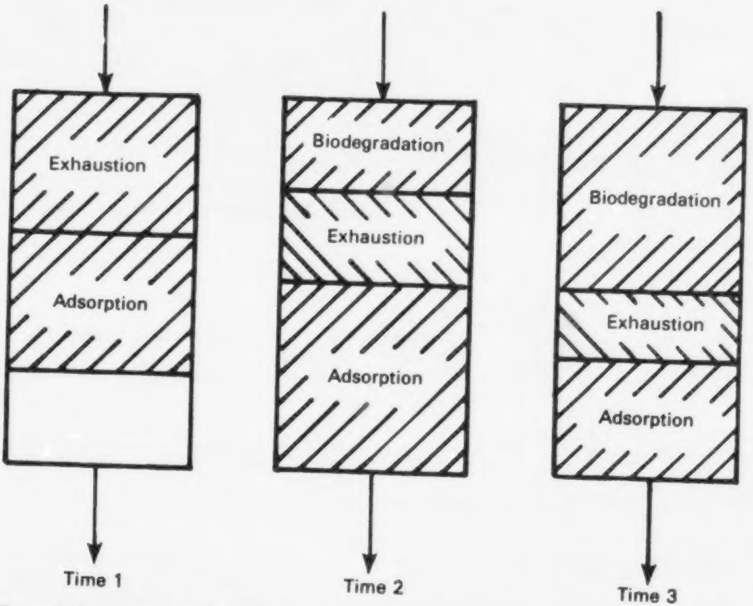


Figure 28. Depiction of three zones of activity in activated carbon adsorbers when microbial activity is significant. At Time 1, microbial activity has not developed because the substrate concentration external to the carbon particles is still low. At Time 2, biodegradation is increased in the upper region where substrate is available. The exhausted zone below will soon become bio-active; the adsorption zone has been forced lower in the bed as exhaustion occurs. At Time 3, breakthrough of organic compounds, due to exhaustion of adsorption capacity, begins. Breakthrough will not be complete because the biodegradation zone will increase and account for a final steady-state removal condition.

biodegradation. It should be stressed, however, that such predictions do not assume *in situ* regeneration, i.e. that the sorbed substrate becomes available to the biofilm; instead, bioactivity results only from substrate external to the particle.

Sontheimer's research group continued practical testing of the combined biodegradation-adsorption process at the Mülheim water works[84]. This project was reported widely in the United States literature. It marked the beginning of United States interest in this process for water treatment. An important aspect of the Mülheim study was the replacement of prechlorination (used to achieve ammonia removal by breakpoint chlorination) with ozonation prior to GAC adsorption. Sontheimer stated that this process change was very important to the success of biodegradation on the surface of GAC because ozone was able to partially oxidize organic contaminants such that the end-products were more biodegradable than the parent compounds. Pre-ozonation extended the service time of GAC beds significantly at the Mülheim plant. These results not only suggest a beneficial effect of ozonation, but also a detrimental effect of prechlorination in that the chlorinated products seemed to be less biodegradable.

Following the success at Mülheim with pre-ozonation, there were also reports in the United States literature on other European plants in Switzerland[72] and in France[85] where this process has extended GAC service time. The EPA recognized that such a process development could have a significant impact on the strategy adopted in the United States for removal of trace contaminants, especially if humic

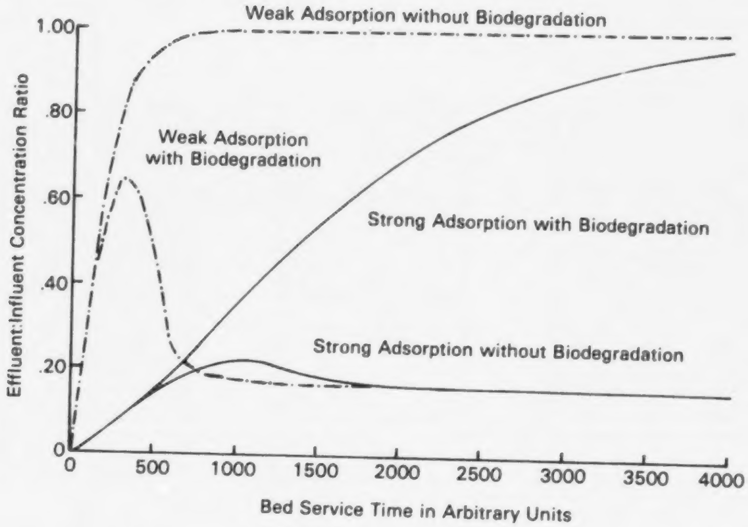


Figure 29. Predicted effluent concentration as a function of service time with the GAC bed. The effect of biodegradation on removal of both weakly and strongly adsorbable organics is shown (After Ying and Weber[81].).

substances, the precursors to THM's, must be removed. Indeed, EPA's initial studies[25] confirmed the European claim that ozone enhanced removals on GAC as shown in Fig. 30. The removal of THM precursors, as represented by TTHMFP, was definitely improved by ozonation, especially as the steady-state removal stage was reached. However, more careful studies suggested that the non-adsorbent surface of sand was just as efficient as GAC in promoting biodegradation[86]. In fact, when ozonation was followed by sand filtration and GAC adsorption, the benefit of ozonation (in terms of enhanced removal of THM precursors) occurred only through the sand filtration process. This leaves in doubt the role played by GAC in enhancing biodegradation. Definitive, pilot plant studies are now underway at the Philadelphia water works to answer this question[35].

There is still little data available on the benefits of microbial activity on GAC in terms of reducing the concentrations of specific organic contaminants. Perhaps the most valuable insight is given by EPA studies of wastewater reclamation at Water Factory 21 in Orange County, California. Here, McCarty, et al.[87] showed that significant biodegradation was occurring in terms of the overall organic parameter, TOC. More important, he compared the removal of trace contaminants by GAC in service for a very long time (referred to as "old GAC") with that by fresh GAC. Many of these contaminants were removed about as well by "old GAC" as fresh GAC. This suggests that when adsorption capacity becomes exhausted, biodegradation can be a fairly effective removal process.

Influence of Pretreatment

Awareness of the inter-relationship between chemical pretreatment and adsorption emerged in the 1970's. In United States practice, it is the combination of chemical coagulation and adsorption which will determine the effectiveness of removal of organic contaminants, while in European practice, it is chemical coagulation, ozon-

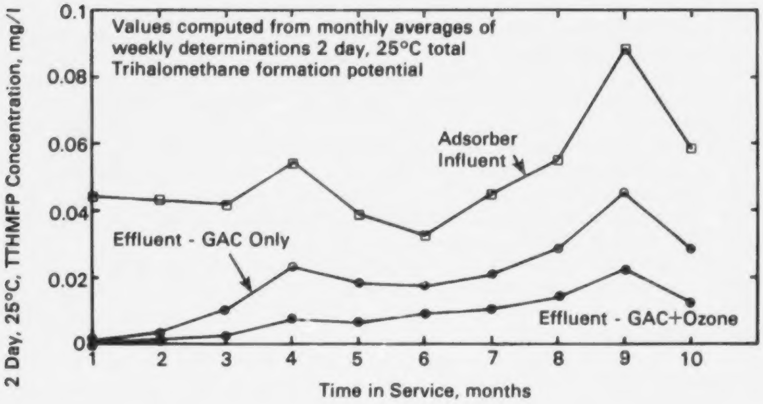


Figure 30. Influence of ozonation prior to adsorption on trihalomethane formation potential removal[25].

ation and adsorption. The work of Lee and Snoeyink[38], Weber, et al.[40] and Randtke and Jepsen[41] in the United States showed very clearly that certain fractions of humic substances are removed by coagulation thereby improving the adsorbability of the remaining fractions. They demonstrated also that the residual inorganic coagulant itself in some way aided in adsorption of the remaining humic substances by activated carbon. The practical implication of these findings is that pretreatment by coagulation may be controlled to achieve optimal removal of the residual THM precursors by adsorption.

Ozonation produces several effects on organic removals which may not always be advantageous. Although still not well documented scientifically, there is evidence that ozonation improves the biodegradability of the organic matter found in many raw water supplies[84,88,89]. There is also evidence that it aids in the flocculation of humic substances. On the negative side, ozonation has been shown to reduce the adsorbability of organic matter when measured by TOC or UV absorbance [90,91]. This may seem logical considering that ozonation leads to more polar by-products which tend to be less adsorbable. The more recent findings from the pilot and full-scale testing at the Mülheim water works suggest that enough ozonation is needed to enhance biodegradation, but that too much ozone will reduce the overall removal efficiency of GAC beds because of the detrimental effect on sorptive capacity[89]. A similar conclusion had also been reached by Benedek[91] in an earlier study conducted at a water works in France.

STATE OF THE ART

Existing Adsorption Systems

A 1977 survey conducted by the Organic Contaminants Committee of the AWWA indicated that only 12 of the 500 plants queried used GAC[92]. In most of these cases GAC replaced sand in filters to provide the dual function of filtration and adsorption. The most notable examples are plants at Mount Clemens, Michigan[25], Davenport, Iowa[25], Lawrence, Massachusetts[25] and Pittsburgh, Pennsylvania[93]. Such GAC beds, however, do not allow sufficient contact time to remove precursors to THM's or to remove other synthetic trace contaminants. Rather, they are mainly designed to remove taste and odor causing compounds and in some cases, pesticides. Moreover, aside from three current EPA demonstration projects, there are no GAC facilities in the United States which include on-site regeneration. In fact, it has been standard practice in the United States to operate GAC beds for three or more years before replacing the media; obviously, such an operating mode severely limits contaminant removal capabilities.

The data base on removal of trace contaminants by GAC beds in the United States should be expanding rapidly as results from full-scale studies at Cincinnati, Ohio; Manchester, New Hampshire; Jefferson Parish, Louisiana; and Passaic, New Jersey, become available. In addition, the Ohio River Valley Sanitation Commission (ORSANCO) is planning four more full-scale tests[75].

In Europe, GAC is a common unit operation for removal of trace organic contaminants and has been used extensively as is shown in Table 5. While most of these plants include pre-ozonation, this was not necessarily intended as a pretreatment for GAC. In most cases, preozonation actually originated out of concern for oxidizing iron and manganese which were frequently present in groundwater, or in blends of groundwater and river water pretreated by river bank filtration. In addition, an apparent aversion of European consumers to the taste of chlorine has fostered ozone treatment to provide disinfection. Only very small dosages of chlorine are applied at the very end of treatment to provide what is known as "safety chlorination", i.e. protection from regrowth of bacteria in the distribution system.

Up until about 1970, the traditional role of activated carbon in European practice, as in the United States, was removal of taste and odor. However, the growing problem of pollution of the Rhine, Ruhr and other major rivers forced consideration of adsorption for removal of a wider spectrum of contaminants. Because few treatment plants used chlorine as the major disinfecting agent, the problem of THM's and THM precursors was not central to the decision in Europe to include GAC beds. Instead, performance criteria were developed which were based on more general parameters indicative of organic contamination. This will be discussed later.

Process Design

The continuing explosion of information which started in the 1970's makes state-of-the-art assessment of process design for GAC beds a moving target. The European experience became very important when the EPA took on the task of preparing a regulation for control of synthetic organic contaminants. As a result, the late 1970's became a period of intense information exchange between Europe and the United States. This began with EPA's translation of proceedings of a special conference on adsorption techniques[94] held at the University of Karlsruhe, Germany in 1975 and with a review of German experience by McCreary and Snoeyink[95] in 1977. Later, the EPA joined with the NATO Committee on Challenges of Modern Society to sponsor two conferences: Oxidation Techniques in Drinking Water Treatment and Practical Applications of Adsorption Techniques in Drinking Water. Some of these papers have since been published in the *Journal of the American Water Works Association.* There was also a special symposium on the adsorption process sponsored by the American Chemical Society[96]. More recently, the USEPA published a treatment document as required for the Trihalomethane Regulation[64]. This document is a state-of-the-art review of treatment techniques, including adsorption, for control of both THM's and their precursors.

Sontheimer summarized the design criteria problem by stating that there is still no way to postulate rules for controlling GAC bed performance or for selecting the type of GAC to be used which may hold for all water works[71]. He proposed, however, the following guidelines: (1) regeneration before the displacement effect produces outlet concentrations of poorly adsorbed components which exceed inlet concentrations; (2) removal of at least 50 percent of the UV absorbing material; (3) identification and monitoring of some specific compounds which are nearly always in the raw water;

Table 5. European Water Treatment Plants Employing GAC[75]

Locations	Capacity ML/day	Capacity MGD	Preozonation
France			
Rouen	38	10	yes
Morsang	118	31	yes
Vigneux	38	10	no
Viry-Chatillon	76	20	no
Federal Republic of Germany			
Mülheim	38	10	yes
Dusseldorf 1	148	39	yes
Dusseldorf 2	68	18	yes
Dusseldorf 3	91	24	yes
Benrath	118	31	yes
Duisburg	57	15	yes
Frankfurt			
Langenau	156	41	yes
Wiesbaden			no
Susel	23	6	yes
Solingen	1.5	0.4	yes
Siegburg	53	14	yes
Duren	28	7.4	yes
Albstadt	14	3.7	yes
Konigswinter	3.8	1.0	yes
Friedsrichshafen	23	6	yes
Stolberg	23	6	no
Vallender	4.5	1.2	no
Stuttgart	66	18	no
Switzerland			
St. Gallen	46	12	yes
Arbon	23	6	yes
Biel	28	7.4	yes
Zurich	194	51	yes
Kreuzlingen	25	6.6	yes
The Netherlands			
Rotterdam	163	43	yes

(4) measurement of the extent of biological activity in the GAC bed; and (5) selection of carbon types based on tests of performance on the raw water itself and on spiked samples.

The practical design specifications proposed by Sontheimer as a result of European experience with GAC for different functions are given in Table 6. It is obvious that removal of synthetic contaminants (see entry in Table entitled "Organic Removal") requires a longer contact time and shorter period between regenerations than removal of taste and odor compounds. The adaptation of a biologically active GAC process (see entry in Table entitled "Biological Activated Carbon") according to Sontheimer lengthens the service time (and thus the period between regeneration) by a factor of four but does require significantly longer contact times (15 to 25 minutes vs 8 to 15 minutes for adsorption only).

Table 6. Design Criteria for GAC Filters in Germany[71]

Treatment Method	Filtration Velocity m/hr	Bed Height m	Empty Bed Retention Time min	Throughout Ratio Before Regeneration* m^3/m^3
Dechlorination	25-35	2	2-4	1,000,000
Taste & odor removal	20-30	2-3	8-10	100,000
Organics removal	10-15	2-3	8-15	25,000
Biological activated carbon	8-12	2-4	15-25	100,000

*m^3 of water processed per m^3 of activated carbon.

This information exchange clearly shows that treatment objectives, design criteria and process performance measures are not sufficiently pinpointed in European practice to satisfy the EPA's need for regulation purposes in the United States. In general, the concern in Europe is protection from synthetic organic contaminants as determined by easily measured parameters such as TOC, UV absorbance, or total organic chlorine (TOCl). In contrast, EPA regulations would probably call for measurement of specific contaminants and regeneration of GAC when certain maximum limits are reached. This more legalistic approach presents problems in establishing design criteria which do not actually require pilot plant studies at the site of a proposed treatment facility.

At EPA's request, the National Academy of Sciences' Safe Drinking Water Committee initiated in 1978 a critical review of the state-of-the-art. With respect to efficiency of adsorption in controlling toxic organic contaminants, the committee concluded that GAC is a particularly effective adsorbent for a wide spectrum of contaminants and supported its use where certain contaminants are known to pose a health risk[24]. There is no evidence to suggest any detrimental effects from the process. However, areas cited as needing further evaluation are: control of bacterial contamination of the treated water (resulting from microbial activity of GAC); identification of any metabolic end-products from microbial activity; documentation of the effectiveness of regeneration after many cycles; and investigation of possible catalytic reactions on GAC which could produce toxic end products. With regard to this last point, EPA-sponsored research has shown that when chlorine and humic substances are introduced into GAC beds, no new chlorinated organic compounds are produced[97]. Other possible precursor compounds remain to be investigated, however.

Selection of Activated Carbon

Although there is no method for "designing" an activated carbon to meet a specific treatment objective, several studies in the 1970's indicated the importance of adsorbent selection. Fig. 31 shows that adsorption profiles can vary within GAC beds containing different adsorbents. In this case, the most hydrophobic carbon (carbon L) gave the best removal of the rather polar, bis 2-chloroisopropyl ether molecule. Other carbons showed definite signs of displacement of this compound.

Another example is the widely varying performance of different activated carbons tested at Louisville, Kentucky when evaluated on the basis of adsorption of chloroform (Fig. 32). Here, exhaustion of sorptive capacity is indicated by the decreasing slope of these plots as the volume of water treated increases. The better removals

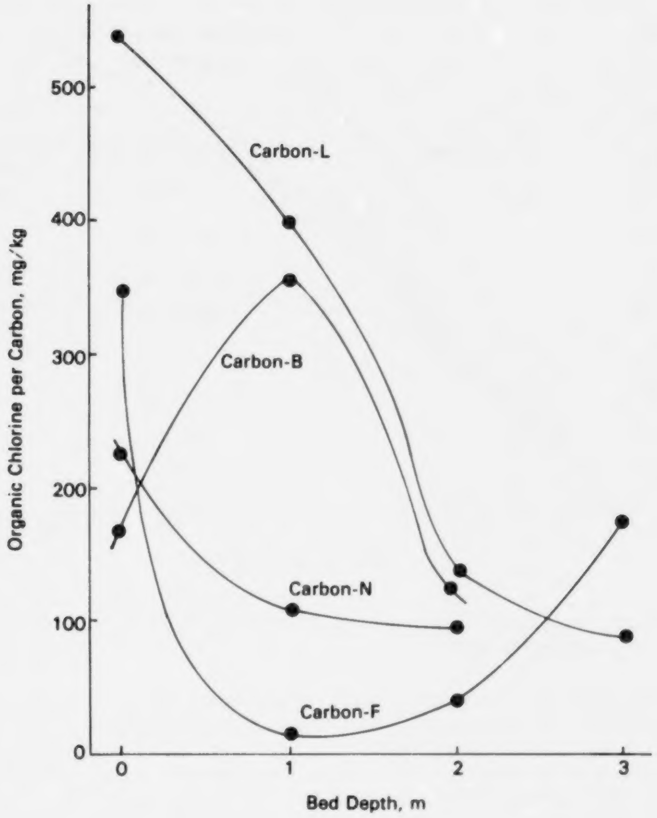


Figure 31. Adsorption of Bis(2-chloroisopropyl) ether on various activated carbons at different filter depths[95].

were obtained with carbons having the larger fraction of smaller pores; these probably excluded competition with humic substances. In contrast, if TOC removal were the design objective, then these carbons would be the least effective (see also earlier discussion of adsorption of humic substances).

The problem of selecting an activated carbon is therefore quite difficult in treatment situations where prechlorination is practiced because both THM's and unreacted THM precursors, i.e. TOC, may need to be removed; one carbon type does not appear optimum for both. Breakthrough of one or the other classes of compounds will control service time as was amply illustrated by EPA pilot plant studies at Miami, Florida[99].

Costs

In anticipation of a regulation requiring GAC treatment at many locations in the United States, the EPA has developed extensive cost estimating procedures and has made these available to design engineers in a format which allows for simple updating and adjustment for specific situations[100]. Important design options are included

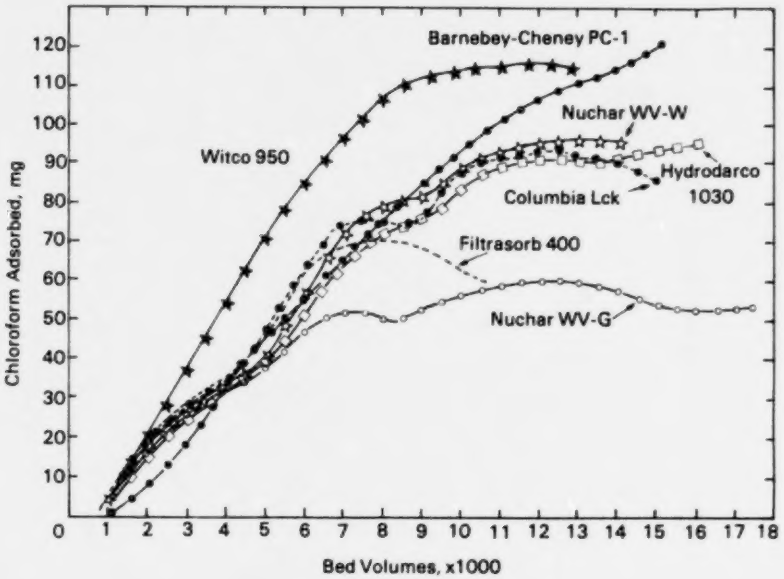


Figure 32. Cumulative adsorption of chloroform by seven brands of granular activated carbon[98].

such as on-site vs. off-site regeneration; frequency of regeneration; size of contactors, i.e. EBCT; pretreatment with ozone vs. no pretreatment; and sand replacement vs. separate post filter adsorbers. As an example, the amortized capital costs, operating and maintenance (O&M) costs and the total costs are compared for sand replacement and separate adsorbers in Table 7 for plants of several sizes. The table shows that total cost is quite sensitive to the size of the plant. A 5 MGD filter adsorber facility would cost 25.3 cents per thousand gallons while a 100 MGD facility would be 12.3 cents per thousand. Post filter adsorbers are more expensive than sand replacement because of the higher capital costs required for constructing the bigger contactors. The percentage increase in cost of water treatment by addition of GAC treatment is anywhere from 43 percent for a small plant (one MGD capacity) to 21 percent for a large plant (100 MGD capacity).

Another important assumption in cost estimation is the regeneration frequency (Fig. 33). Total costs are seen to rise very sharply as the regeneration frequency increases, i.e. as the time interval between regenerations shortens to less than about two months. These results are also dependent upon the assumptions used in estimating carbon loss rate. While available data for more than a few cycles are limited, an assumption of 6 percent loss for post filter adsorption and 10 percent for sand replacement seems reasonable.

Process Control

The basic objective in process control is to determine when to regenerate. Given the broad choice of treatment objectives discussed, it is clear that monitoring of performance will depend on which organic contaminants have been selected for reduction. The greater the specification of target trace contaminants, the more expensive is monitoring and the less likely is real-time control. The success of a monitoring pro-

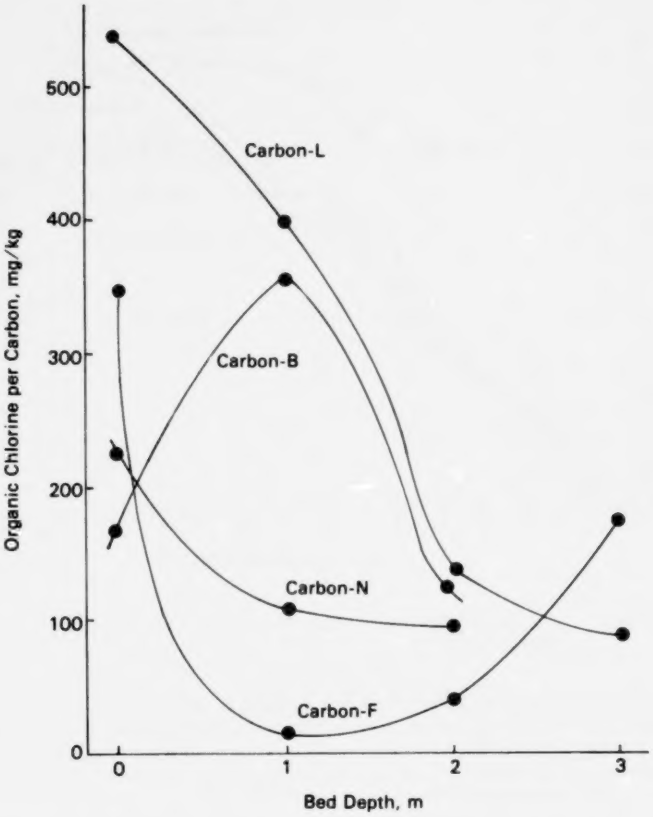


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Table 7. Amortized Capital and O&M Costs for GAC Systems[100]

Design Capacity		Amortized Capital Cost				O&M Cost				Total Cost			
		Sand Replacement		Filter Adsorber		Sand Replacement		Filter Adsorber		Sand Replacement		Filter Adsorber	
ML/day	MGD	¢/kL	¢/1000 gal	¢/kL	¢/1000 gal	¢/kL	¢/1000 gal	¢/kL	¢/1000 gal	¢/kL	¢/1000 gal	¢/kL	¢/1000 gal
3.8	1	6.4	24.8	7.6	29.4	5.1	19.5	5.8	22.1	11.5	44.3	13.4	51.5
19	5	2.3	9.0	3.3	12.7	3.4	13.0	3.3	12.8	5.7	22.0	6.6	25.3
38	10	1.6	6.2	2.8	9.8	3.0	11.7	2.8	10.8	4.8	17.9	5.4	20.8
380	100	0.5	2.0	1.3	4.9	2.3	8.7	1.9	7.4	2.8	10.7	3.2	12.3
570	150	0.4	1.7	1.2	4.6	2.2	8.4	1.8	7.1	2.8	10.1	3.0	11.7

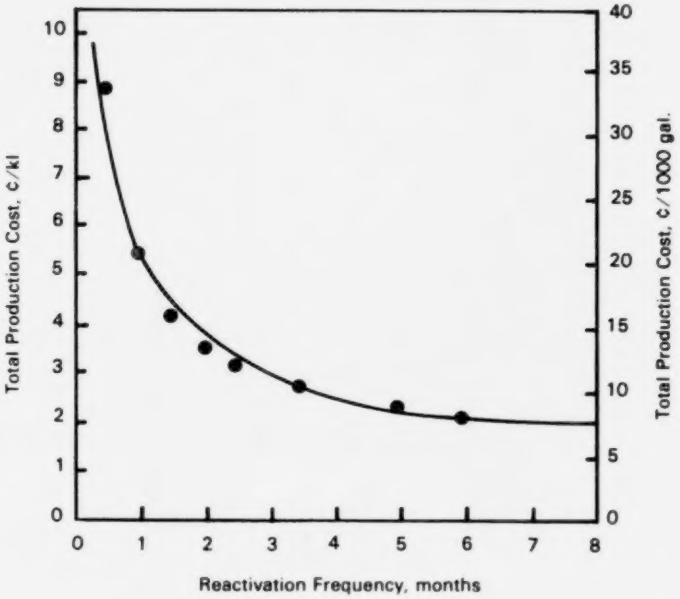

Figure 33. Total production cost versus reactivation frequency in months for 380-ML/day (100-mgd) post-filter adsorption[100].

gram also depends on the sampling frequency. This is especially important where accidental spills may occur.

Suffet[24] recommended that sophisticated GC/MS (gas chromatography/mass spectroscopy) be used for confirmation purposes only and not for routine assessment of performance. In research this technique has proven very useful in demonstrating the level of effectiveness of GAC in removing many contaminants[35,45,63].

Non-specific organic analyses are used in European practice, the most common of these being UV absorbance (which measures aromatic compounds), TOC (which measures the background compounds such as the humic substances) and TOCl (which measures the total organic chlorine contained in organic compounds). The TOCl test was originally developed at the University of Karlsruhe by Kühn and Sontheimer[101] with the aim of measuring compounds containing organic chlorine which had been adsorbed in full-scale operation of activated carbon beds. Procedures were then developed and tested in the EPA laboratories by Dressman, et al.[102] such that the organohalide content of water samples themselves could be measured. Inclusion of all halogenated forms led to adoption of the term total organic halogen (TOX) to describe the test. Still later, Jekel and Roberts[103] modified the TOX test to distinguish between purgeable (i.e. more volatile) and non-purgeable (i.e. less volatile) organohalides.

Although TOX measurements of the influent and effluent of GAC beds may be useful as a general guide to performance, the variability in concentrations of individual compounds limit interpretation of results. Alternatively, measuring the loading of sorbed TOX allows estimation of the position and shape of the active adsorption zone and the remaining service time of the bed. A recent example of use of this technique is presented by Quinn and Snoeyink[104] in their EPA-sponsored work at the Jefferson Parish, Louisiana, full-scale GAC facility (Fig. 34). The buildup in

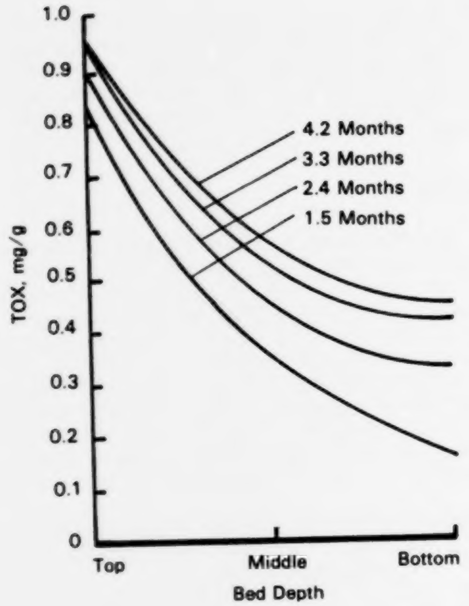

Figure 34. Jefferson Parish adsorber TOX profiles[104]

sorbed TOX along the bed length as service time increases from 1.5 to 4.2 months is seen very clearly. What is still needed, however, is a method to correlate such data with effluent quality.

The concern over THM's in the United States implies not only a need for their removal, but control of their precursors compounds, the humic substances, before the chlorination step[64]. Hence, another measure of process performance is reduction of THMFP. For plants practicing prechlorination as well as post chlorination, both the THM and THMFP test are needed. The difficulty of the THMFP test is that it must be carried out over several days in order to provide sufficient time for the chlorine to react with the humic substances. Thus, it does not lend itself to real-time process control. An alternative parameter which it was hoped could be correlated with the THMFP test is non-purgeable organic carbon (NPOC)[25]. This seems logical because humic substances represent most of the organic carbon in a raw water. Plant studies at Jefferson Parish, Louisiana[36] supported this argument but, unfortunately, similar studies at Miami, Florida[33] did not. The NPOC parameter, however, still has utility as a general indicator of adsorption efficiency.

Test procedures are also needed to assess the effectiveness of on-site carbon regeneration. These must not be limited to the more traditional measures such as density and iodine number. Rather, they must include some way of evaluating the effectiveness of the regenerated carbon in adsorbing specific contaminants of concern to a water works.

Sontheimer, at the University of Karlsruhe, has collaborated with several of the major German water works over many years to develop new practical test procedures. Central to most of these is the use of UV absorbance and DOC (dissolved organic carbon) as measures of the general makeup of organic contaminants. The tests include determination of adsorption rate, adsorption equilibrium and response to competitive adsorption. In addition, there has been progress on use of the thermogravimetric balance. This device measures the rate of weight loss of the activated carbon as a function of regeneration temperature. The rate of weight loss can be correlated with removal of sorbed organic compounds; when used conjunctively with GC/MS, it may even be possible to determine which compounds are removed. A major objective of all these procedures is development of simple ways to monitor GAC performance.

A Look to the Future

Although not promulgated, the regulation proposed by the EPA in 1978 to control synthetic organic contaminants by GAC was very important. It precipitated a scientific debate over the merits of the adsorption process which focused attention on the gaps in present understanding. The direct consequence has been research that is extending our knowledge of the principles of adsorption and is demonstrating through pilot plant and full-scale studies, practical applications of the process. These efforts are fostering a better understanding of the process and its widespread utility, and also of its limitations. It would seem that the case for GAC as the best adsorbent for removal of a broad spectrum of organic contaminants has been made quite clearly. All that remains is to arrive at an acceptable way of recommending its use in United States water works without overspecifying process design and performance criteria.

EPA-funded pilot plant and full-scale demonstrations in the late 1970's certainly did much to close the gap between adsorption theory and practice. Nevertheless, the need for more basic research persists. Prediction of adsorber performance is one area in which research could have very practical consequences. It could in particular lessen the need for long and expensive pilot plant testing programs. However, the variability in chemical composition of raw waters from site to site, and from season to season at any given site, is a great barrier to adaptation of mathematical modeling principles. The most ideal predictive technique would allow estimation of service time based solely on knowledge of the mix of organic contaminants present at a given time. This may be possible as progress is made in prediction of equilibrium adsorption behavior by such procedures as those developed by McGuire and Suffet[27], Manes[28], Belfort[29], and Weber and van Vliet[30], all of which were described earlier.

The rate at which adsorption equilibrium takes place is equally important. The work of teams led by Weber, Snoeyink, and Sontheimer advanced knowledge in this area, particularly by recognizing the importance of surface diffusion and by distinguishing the slow rate of adsorption of humic substances from the more rapid rate of trace contaminants. This should allow for better assessment of process dynamics in GAC beds as these two categories of compounds compete for adsorption sites.

Two relatively unexplored areas of research on the topic of adsorption rate involve the influence of surface topography (i.e. particle shape and roughness) and macro-micropore diffusion. The recent work of van Vliet, et al.[105] shows that higher external film, mass transfer coefficients are associated with adsorption on activated carbons than on carbonaceous resins; concomitantly activated carbons have rougher surfaces. Their work also suggests that internal surface diffusion cannot explain the observed slow approach to equilibrium in fixed-bed adsorbers. Instead, they draw upon past findings of other researchers which indicate internal mass transport to consist of: (1) rapid migration through macropores and (2) slow migration through micropores. Evidence of a renewal of interest in this concept is noted in the recent research of Peel and Benedek[106] and Famularo, et al.[107] in which mathematical models are developed.

Modeling will probably never be a panacea in predicting the breakthrough behavior of each and every contaminant to be removed. Nevertheless, it may provide a means for bracketing the expected performance if a way can be found for subdividing the contaminants logically into several large classes. In this regard, the development of new analytical methods may be of considerable help. For example, it is already possible to separate purgeable, and thus more volatile, from nonpurgeable, and thus less volatile, organic compounds; these categories can be measured either by organic carbon or halogen content. The research group at the University of Karlsruhe is working on such an approach for characterization of the adsorptive behavior of organic mixtures according to such broad classes of compounds.

The beneficial aspects of microbial degradation on adsorbent surfaces used in water treatment needs to be examined more closely. At present, there is limited understanding of the interaction between biodegradation and adsorption, particularly as it relates to removal of specific trace compounds found in water treatment. Just how sorbed substrates can again become available to the microbial population of a GAC bed is poorly understood, although there is evidence of "back diffusion" from the internal surfaces to the external surface[108]. Assessment of rules governing biodegradability of synthetic organic contaminants especially at low concentrations is also needed, as is better understanding of the metabolites produced and their fate in the GAC bed.

Such research can lead to improved design of GAC beds. For example, if biodegradation is an important feature, then the type of pretreatment to be provided needs to be specified more carefully (perhaps ozone should be used); also, the flowrate through the bed and the adsorbent particle size may need to be optimized to take advantage of biological rather than adsorptive principles. Process control, too, would reflect concern over minimizing the release of bacteria into the effluent; one method, for example, would be by more frequent backwashing. EPA pilot plant studies now underway in Philadelphia, Pennsylvania[35] should shed more light on all these areas.

The development of carbonaceous resins in the 1970's showed how advances can be made in designing new adsorbents and in improving old adsorbents. Past research has shown that not all contaminants are removed to the same extent by activated carbon. Therefore, other adsorbents may be important in very specific situations, as may be the case in treatment of contaminated groundwater, for example. The contrasting adsorptive behavior of humic substances and low molecular weight, halogenated compounds shows quite clearly the importance of pore size distribution. Manipulation of pore size distributions and activation procedures (for activated carbons) may both lead to development of better adsorbents.

As removal functions to be performed by adsorbents become more specific there is need to review the minimum standards for judging acceptability of adsorbents. The old standards[109] adopted by the AWWA in 1974 need to be revised to include better performance indicators for removal of trace organic compounds of concern in practical situations. A committee of the AWWA is working on this problem.

Efficient and economical on-site regeneration is also essential for wide acceptance of the adsorption process. Ongoing pilot plant studies at Cincinnati, Ohio and Manchester, New Hampshire using the fluidized bed furnace and at Passaic Valley, New Jersey using the infra-red furnace should answer the need for practical data. Most important is the use of activated carbon over the number of cycles corresponding to that estimated by loss rate per cycle; at a 6 percent loss rate, this would be about 16 cycles.

In looking to the future, it is interesting to reflect on discussions by eminent scientists and engineers[110] at the 1958 Conference on "Man Versus Environment." At that time, the little known area of organic contaminants was recognized as a potential major concern of the future. Since then, as a result of the introduction of more sophisticated analytical techniques, our perception of the problem has sharpened, but, it must be said a specific control strategy has yet to be adopted for use in the United States. However, GAC adsorption has emerged as the control strategy with the most likely chance of success based on its effectiveness and costs. Other adsorbents with further development, may also prove advantageous in control of special problems, e.g. those associated with treatment of groundwater. Advances in the understanding of adsorption phenonema will surely lead to improvement of water treatment practice. It requires no special insight to foresee that removal of organic contaminants will generally require use of a separate unit for this purpose. This process, like coagulation, sedimentation, filtration, and disinfection, will be viewed as an essential component of the conventional water treatment plant.

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REMOVAL OF ORGANIC SUBSTANCES FROM WATER BY AIR STRIPPING

Perry L. McCarty, PhD

INTRODUCTION

The value of aeration for improving the quality of water has long been known, and this process was among the first to be used for water treatment. As early as 1887, Charles B. Brush reported in the *Journal of the New England Water Works Association*[1] that "The necessity of aeration even in Europe. . .is now being recognized and its necessity advocated." Use then, and indeed at the present time, has been primarily for aesthetic purposes, to reduce the level of tastes and odors in water. Initially, this improvement in water quality was believed to result primarily from the introduction of oxygen, but later, the benefits were better understood as the result of the removal of volatile compounds.

In his book published in 1935 on *Elimination of Taste and Odor in Water*[2], John R. Baylis described many of the principles of aeration and its applications to the treatment of water supplies. He indicated that aeration was a well established practice, and was then in use at an estimated 300 water supplies in the United States. He suggested that use of aeration was not confined to taste and odor removal, but was valuable for adding oxygen to water, and for removal of iron, manganese, and carbon dioxide. He also suggested that many inorganic and organic compounds which might be responsible for tastes and odors in water could be removed by aeration, and he provided boiling point and solubility data then available for a large number of organic compounds, some of which are of toxicological concern today, to aid in assessing the potential effectiveness of stripping with air in removing them. Thus, the value of this process for stripping trace organic substances was recognized as early as 1935.

By 1958, a United States Public Health Service survey[3] indicated that 2,154 water treatment plants had aerators. However, the American Water Works Association's third edition of *Water Quality & Treatment*, published in 1971[4], suggested that aeration was generally not an efficient method for the removal or reduction of unpleasant tastes and odors because most of the substances causing these traits were not sufficiently volatile. It was indicated that a number of plants had discontinued using aeration for taste and odor reduction, and that aeration was then used primarily for iron and manganese removal. Use of aeration for well waters was also

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questioned because of possible contamination by airborne impurities including pathogens. Thus, emphasis on the beneficial effects of aeration in more recent times seems to have declined.

However, in 1977, air-stripping was found to be effective for removing a wide range of volatile organic materials present in trace concentrations in reclaimed wastewaters[5]. It was pointed out that many potentially toxic materials, that were not effectively removed by activated carbon treatment, or that broke through activated carbon beds most readily, could be removed efficiently by aeration. This and subsequent studies[6-11] indicated that many of the organic contaminants being found in ground as well as surface waters could be effectively removed by air-stripping. Thus, the potential value of this relatively inexpensive treatment process for dealing with specific classes of potentially harmful organic compounds was demonstrated. For this reason, it is desirable to re-evaluate this old process for application to the newer problems of today.

PRINCIPLES OF REMOVAL BY AIR-STRIPPING

General

A description of air-stripping principles and their employment in process design cannot avoid use of equations. The examination presented herein, therefore, depends more or less heavily on equations which, while familiar for many, may seem arcane to others. To assist in understanding these principles, some terms that are widely used in gas exchange phenomena are defined:

Mass Transfer—

Mass transfer refers to the movement of a given mass of a compound from one point to another within a given medium, or from one medium, such as water, to another medium, such as air . Transfer of mass between media or between phases is the objective of air-stripping. In this case the transfer of mass takes place across a boundary that exists between the two phases, and this boundary can be characterized by its area. In order to design a stripping process, it is necessary to understand the factors that affect the rate at which the compound of interest moves across this boundary, and this is generally expressed as the net movement of contaminant mass per unit area of boundary per unit of time. This is referred to here as the rate of mass transfer.

Diffusion—

Diffusion is one of the processes by which a compound moves from one point in a given medium to another. This is a molecular process and results from the normal movement of molecules, their random collision with one another, and the tendency towards an even mixing of the molecules that results. The process of diffusion tends to move a compound from a point of high concentration within a medium towards one of lower conentration. This difference in concentration divided by the distance between the two points is termed the concentration gradient; the rate of mass transfer between the two points by diffusion is proportional to this concentration gradient. The proportionality constant is termed the coefficient of diffusion. There is a relationship between diffusion and mass transfer, and this will be discussed later in some detail.

Henry's Law—

Henry's law is a statement relating the concentration of a given compound in air to its concentration in water under conditions of equilibrium. An understanding of Henry's law is basic to an understanding of air stripping as will be indicated in the following.

Equilibrium Considerations

Henry's law states the relationship that exists between the amount of a volatile substance in the gas phase above a liquid and the amount of the substance dissolved in the liquid at a given temperature and at equilibrium. For an ideal volatile compound which obeys this law, the relationship is given by:

$$H_i = F_{ie}/C_{ie} \tag{1}$$

where H_i is the Henry's law constant, F_{ie} is the partial pressure expressed as a concentration (mg/m^3) of compound i in the gas phase above the liquid, and C_{ie} is the concentration in the liquid (mg/m^3), under conditions of equilibrium between the liquid and the gas phases.

If the relative concentrations of the compound in the liquid and the gas phases are not in equilibrium as indicated by Henry's law, then the gas will tend to move from one phase to the other in a direction to approach equilibrium. Volatile organic materials dissolved in water can be removed from water by transfer to a gas such as air if the concentration in the air is below the equilibrium value with the water phase. Thus, Henry's law provides the basic equilibrium foundation for determining the removability of volatile organic materials from water by air-stripping.

As with other equilibrium constants, the Henry's law constant varies with temperature, and for the case where the enthalpy of dissolution remains relatively constant, the temperature dependence is given by:

$$\log H_i = \frac{\triangle H_i^\circ}{2.3\ RT} + K_i \tag{2}$$

where,

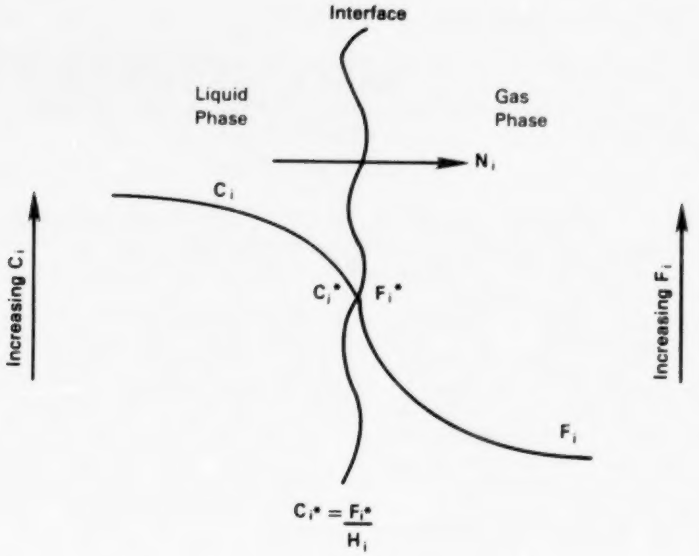
$\triangle H_i^\circ$ = the standard enthalpy of dissolution for gas i (joule/mol)
R = universal gas constant (8.314 joules/deg mol)
T = absolute temperature, K
K_i = constant

In general, H_i increases by a factor of two to three for each 10° C rise in temperature. Thus, the temperature effect can be quite significant.

Rates of Mass Transfer

Based upon Henry's law a volatile component can be removed from water by air-stripping if the bulk concentration C_i is greater than the equilibrium concentration with the bulk concentration F_i in the air, that is if $C_i > F_i/H_i$. This condition is shown pictorially in Fig. 1. The mass transfer from water to air then occurs in response to a negative gradient from the bulk water to the water-air interface, across the interface, and then from the interface into the bulk air. Generally it is considered that the rates of transfer from the bulk water to the interface, and from the interface to the bulk air are much slower than the rate of transfer across the interface itself. For this usual case, the interfacial concentration in the water C_i^* is in equilibrium with the interfacial concentration in the air F_i^*, thus

$$C_i^* = F_i^*/H_i \tag{3}$$



Interface
Liquid Phase
Gas Phase
N_i
C_i
Increasing C_i
C_i^*
F_i^*
Increasing F_i
F_i
$C_i^* = \frac{F_i^*}{H_i}$

Figure 1. Transfer of volatile components from liquid phase to gas phase in response to a concentration gradient.

The rates of mass transfer from the water to the interface and from the interface into air are given by the following:

$$N_i = K_{iL}(C_i - C_i^*) \qquad (4)$$

$$N_i = K_{iG}\ (F_i^* - F_i) \qquad (5)$$

where,

N_i = The rate of mass transfer (mg/m^2/sec)
K_{iL} = Overall liquid transfer coefficient (m/sec)
K_{iG} = Overall gas transfer coefficient (m/sec)

The rate of transfer from the water to the interface must equal that from the interface into the air. By combining Equations (3) and (5) with Equation (4), the general formula for the overall transfer of the volatile component from water to air is found to be

$$N_i = K_i\,(C_i - F_i/H_i) \qquad (6)$$

for which,

$$1/K_i = 1/K_{iL} + 1/H_iK_{iG} \qquad (7)$$

From Equation (7) it can be seen that when H_i is very large, that is when the volatile compound is not very soluble in water, the last term in the Equation is negligible and K_i essentially equals the liquid transfer coefficient. The transfer is then said to be liquid-phase controlled. In the converse situation of very small H_i, the overall transfer coefficient essentially equals H_iK_{iG}, and the transfer is gas-phase controlled. The relationships between water concentration, the air partial pressure and the interface concentration of the volatile component for these different cases are illustrated in Fig. 2.

It is more generally the nature of the volatile component itself rather than the flow conditions which determines whether a mass transfer system is gas-phase or liquid-phase controlled. However, the process design should consider which, if either, phase is controlling. The values for the individual phase rate coefficients are a function of the process characteristics as well as temperature. Thus, for example, if the process is gas-phase controlled, then the process should be designed to achieve a high gas-transfer coefficient. Also, in comparing the effects of process variables on rates of transfer of different volatile components, it is important to know whether or not both are limited by rate of transfer across the same phase. According to Mackay and Leinonen[12] the phase resistances are approximately equal when H_i equals 7×10^{-3}. For values well above this, the liquid-phase transfer would control, and for values well below this, gas-phase transfer would control.

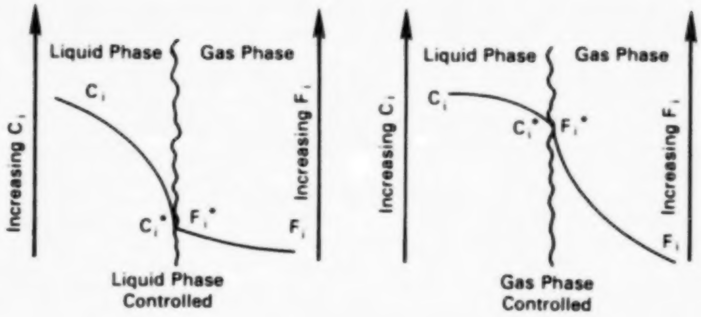
Aeration and air-stripping are commonly used processes for water and wastewater treatment for absorption of oxygen, and for removal of carbon dioxide, hydrogen sulfide, and ammonia. Knowledge of the rates of transfer of these gases for different absorption or stripping systems can be used to evaluate the effectiveness of such systems for removal of volatile organic materials. The physical properties of these gases are listed together with those of volatile organic compounds in Table 1. Oxygen, carbon dioxide, and hydrogen sulfide are relatively insoluble compounds as indicated by high Henry's law constants, while ammonia is very soluble. Because of its low solubility, the absorption or desorption of oxygen is liquid-phase controlled, while the removal of ammonia is for the most part, gas-phase controlled. Experience with absorption of oxygen can thus be used directly for predicting the removal by stripping of low solubility gases ($H_i \ll 7 \times 10^{-3}$) and with ammonia for gases of greater solubility.

In most stripping systems, the interfacial area $\underline{a}$, between phases is not easily determined, but it is the product (K_ia) which is generally needed for design and can readily be determined from empirical studies. The value a represents m^2 of interfacial area per m^3 of reactor volume. If this product is determined for absorption of oxygen in a system, then its value for volatile organic compound removal for the same system can be determined if the relative magnitudes of the diffusion coefficients for oxygen and the compound are known. For diffused air or mechanical aeration systems employing a basin or mixed tank, the product has been shown by Tsivoglou[13] and Rathbun[14] to be directly proportional to the diffusion coefficients:

$$(K_ia) = (K_{O_2}a)(D_{iL}/D_{O_2}) \tag{8}$$

However, for a packed tower stripper, the relationship is generally thought to vary through the one-half power of the diffusion coefficients[10]:

$$(K_ia) = (K_{O_2}a)(D_{iL}/D_{O_2})^{0.5} \tag{9}$$



Liquid Phase Controlled

Gas Phase Controlled

Figure 2. Difference in concentration gradients between liquid and gas phases for liquid phase and gas phase controlled processes.

With gas-phase controlled transfer, the power relationship is intermediate between the two liquid-phase controlled processes[15] as indicated in the following for ammonia:

$$(K_i a) = (K_{NH_3} a)(D_{Gi}/D_{NH_3})^{0.67} \tag{10}$$

The above relationships are valuable for extending the current knowledge of systems for transferring inorganic gases to the removal of volatile organic compounds through air-stripping.

Equations (8) through (10) suggest that for different situations, the rate of mass transfer is a function of the diffusion coefficient to some power which varies between 0.5 and 1.0. From the literature there appears to be some differences of opinion on just what power to use in a particular case, but in any event, the differences in mass transfer which result are generally not as significant in comparative removals of different compounds as is the effect of their Henry's law constants. This will be seen in a subsequent section.

Properties of Hazardous Organic Compounds

As the previous discussion shows, an important property of hazardous organic compounds which governs whether they may be readily removed from water supplies by air-stripping is their Henry's law constant. Such values have not been evaluated extensively, and it is not presently known whether the removability by air-stripping of the many compounds of concern can be described well by the relationship given in Equation (1) over a sufficient range that extends down to the microgram per liter concentration. Therefore, additional evaluation is needed. However, an approximation of the Henry's law constant can be obtained from two properties of organic compounds which are somewhat more readily available: the compound's vapor pressure and its solubility in water. The first expresses the equilibrium relationship between a solid or liquid compound and its gaseous concentration, and the second expresses that between the compound and its concentration in water. If a compound is both at equilibrium with the gas phase and the water phase, then the respective concentrations in the gas and water phases must also be at equilibrium, and thus the ratio of these respective concentrations should yield the Henry's law constant[12],

Table 1. Calculated Henry's Law Constants and Water Diffusion Coefficients at 20°C for Selected Organic and Inorganic Compounds*

Compound	H_i† $\frac{mg/m^3}{mg/m^3}$	D_{iL} cm^2/s $\times 10^5$	Compound	H_i† $\frac{mg/m^3}{mg/m^3}$	D_{iL} cm^2/s $\times 10^5$
Vinyl chloride	270	1.3	1,2-Dichloropropylene	8.3×10^{-2}	1.1
Dichlorofluoromethane	87	1.3	Alpha-BHC	8.3×10^{-2}	–
Oxygen	29	2.4	1,2-Dichlorobenzene	7.1×10^{-2}	0.98
1,1-Dichloroethylene	7.1	1.2	Anthracene	5.8×10^{-2}	–
1,2-Dichloroethylene	7.1	1.2	1,2-Dichloroethane	4.6×10^{-2}	1.2
Trichlorofluoromethane	4.6	–	Hexachloroethane	4.6×10^{-2}	0.97
Methyl bromide	3.9	1.5	1,1,2-Trichloroethane	3.2×10^{-2}	1.1
Toxaphene	2.6	–	Bromoform	2.6×10^{-2}	1.1
Carbon dioxide	1.1	1.9	1,1,2,2-Tetrachloroethane	1.7×10^{-2}	1.0
Carbon tetrachloride	1.0	1.1	Naphthalene	1.5×10^{-2}	0.92
Tetrachloroethylene	9.6×10^{-1}	1.0			
Chloroethane	6.2×10^{-1}	1.3	Fluorene	8.7×10^{-3}	0.86
Beta-BHC	4.6×10^{-1}	0.81	Acenaphthene	7.9×10^{-3}	0.82
Trichloroethylene	4.2×10^{-1}	1.1	Phenanthrene	5.4×10^{-3}	–
Hydrogen sulfide	3.4×10^{-1}	1.8	Bis(2-chloroisopropyl) ether	4.6×10^{-3}	0.80
Methyl chloride	3.3×10^{-1}	1.5	Acrolein	4.0×10^{-3}	1.3
1,2-Trans-dichloroethylene	2.4×10^{-1}	1.2	2-Nitrophenol	3.2×10^{-3}	1.1
Ethylbenzene	2.4×10^{-1}	0.93	Acrylonitrile	2.6×10^{-3}	1.3
Toluene	2.4×10^{-1}	1.0	Di-n-butyl phthalate	2.6×10^{-3}	0.58
1,1-Dichloroethane	2.1×10^{-1}	1.2	2,4-Dichlorophenol	1.7×10^{-3}	–
			4,4'-DDT	1.4×10^{-3}	–
Benzene	1.9×10^{-1}	1.1			
Chlorobenzene	1.7×10^{-1}	1.0	2-Chlorophenol	8.7×10^{-4}	1.0
1,1,1-Trichloroethane	1.5×10^{-1}	1.0	Ammonia	7.1×10^{-4}	2.0
Chloroform	1.4×10^{-1}	1.2	Nitrobenzene	4.6×10^{-4}	1.0
1,3-Dichlorobenzene	1.1×10^{-1}	0.97	Isophorone	1.7×10^{-4}	0.82
			Pentachlorophenol	8.7×10^{-5}	–
Methyl chloride	1.0×10^{-1}	1.4			
Heptachlor	9.6×10^{-2}	–	Dimethyl phthalate	1.7×10^{-5}	0.78
1,4-Dichlorobenzene	8.7×10^{-2}	0.95	Lindane	1.3×10^{-5}	–
Aldrin	8.7×10^{-2}	–	Phenol	1.1×10^{-5}	1.1
1,2-Dichloropropane	8.3×10^{-2}	1.1	Dieldrin	7.1×10^{-6}	–
			4,6-Dinitro-o-cresol	7.1×10^{-6}	–

*For organic compounds, H_i after values from Reference 25 and D_{iL} calculated from Equation 13; for inorganic compounds, H_i are from Reference 26 and D_{iL} from Reference 27.

†H_i expressed for convenience as ratio of mass per unit volume in air to mass per unit volume in water; for more usual units, multiply by 0.024 to convert to atm-m³/mol, or by 1340 to convert to a mol fraction ratio.

$$H_i = F_{is}/C_{is} \tag{11}$$

where

F_{is} = vapor pressure concentration of compound i (mg/m^3) at a given temperature
C_{is} = solubility of compound i (mg/m^3) in water at the given temperature

Values of the Henry's law constant for various organic compounds, especially those on the U.S. Environmental Protection Agency (EPA) priority pollutant list, and for some inorganic gases of significance, are listed in Table 1.

Table 1 lists coefficients for diffusion of the compounds through water and through air. The values for water were for the most part calculated from the Equation by Wilke and Chang[16],

$$D_{iL} = 7.4 \times 10-8(T)(XM)^{0.5}/\mu V_o^{0.6} \tag{12}$$

where

μ = solvent viscosity, centipoise
T = absolute temperature, K
X = association parameter, 2.6 for water
M = solvent molecular weight, 18 for water
V_o = molal volume of solute at normal boiling point, cc/g-mole

Values for V_o were not readily available for the organic compounds of interest. In order to determine the diffusion coefficients listed in Table 1, V_o was roughly estimated to equal the quotient of the molecular weight and the density of the pure liquid chemical at 20°C in g/cm^3. Since the latter would normally be smaller at the boiling point of the compound, the calculated diffusion coefficients are somewhat larger than they should be. Through use of Equation (13), diffusion coefficients for other temperatures can be readily calculated.

AIR-STRIPPING PROCESSES

Types

Stripping of volatile organic components from water into air depends upon bringing the two phases into intimate contact under conditions wherein the forces for stripping will be most favored. This involves maximizing the interfacial area of contact between the two. Various processes for doing this are illustrated in Fig. 3. In diffused air systems, the air stream is broken into small bubbles, providing a large surface area as they rise through water. This is a common procedure for introducing oxygen into wastewaters for biological treatment. Mechanical aeration is also used to produce a similar effect; it results in breaking the liquid into droplets or films which are thrown through the air. As the water splashes back into the basin, some air is also entrained as bubbles and additional transfer takes place. Such processes could be used for removal of volatile organic compounds with mass transfer coefficients and Henry's law constants similar to that of oxygen.

With less volatile compounds, larger quantities of air than normally used for biological treatment may be required to obtain the desired efficiencies of removal, and therefore some type of tower system may be preferred for reasons of economy. In towers the pressure drop for mixing air and water is much less than in a basin. In a

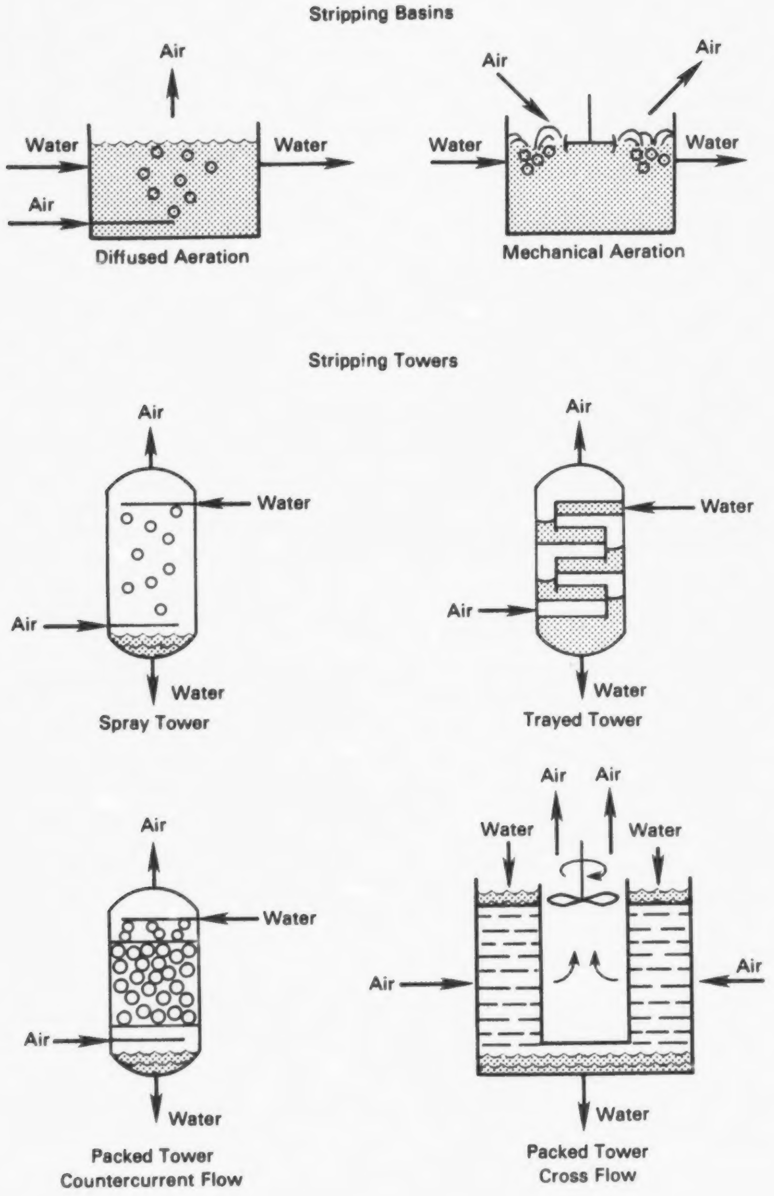

Stripping Basins
Air
Water
Water
Air
Diffused Aeration
Air
Air
Water
Water
Mechanical Aeration
Stripping Towers
Air
Water
Air
Water
Spray Tower
Air
Water
Air
Water
Trayed Tower
Air
Water
Air
Water
Packed Tower
Countercurrent Flow
Air
Air
Water
Water
Air
Air
Water
Packed Tower
Cross Flow

Figure 3. Configurations for different air-stripping processes.

spray tower, air and water flow in a countercurrent fashion. The water is broken into fine droplets by passage through nozzles in order to increase the surface area exposed to the rising air. Power is required to pump the water and force it through the nozzles. Also, some of the water may be carried out with the rising air. Other kinds of tower systems tend to be more efficient both in terms of contaminant removal and energy consumption, although the capital costs may be higher. In a packed tower, water is broken into slow-moving films which form and reform exposing renewed surfaces to the rising air. The counter-current flow of air and water is most efficient for the transfer process. Some towers are built for horizontal or cross-flow of air by falling droplets of liquid. This type of tower has been used for removing highly soluble gases such as ammonia from wastewaters, and has good potential for some of the less volatile organic components. In trayed towers, air is broken into small bubbles and pass up through a volume of water.

Thus, there are many different mechanical processes which can be used for removing volatile organic materials from water. For highly volatile components which require relatively low volumes of air to water, stripping in basins may be the best procedure, while towers tend to be more cost effective if relatively large volumes of air to water are required. When the choice is not critical on process grounds, other factors such as aesthetics, noise, land area, compatibility with other processes or existing facilities, versatility, or other factors may govern the choice.

Considerable experience is available in the water supply and wastewater treatment fields for the introduction of oxygen into water, especially with basin type systems, and this experience together with knowledge of relative transfer coefficients and Henry's law constants can be used to predict the efficiency of removing volatile organic compounds. Towers are widely used in the chemical industry and this experience can be directly applied to the design of air stripping systems for volatile organic removal.

Design Factors Affecting Removal Efficiency

In a stripping system, the area of contact between the air and water is generally not known and cannot easily be measured, thus making design based upon direct use of Equations (4) or (5) difficult. The overall mass transfer, however, can usually be measured and this is proportional to ($K_i a$).

For a given process the factors of importance in the efficiency of removal of a given volatile organic are the Henry's law constant, the relative volumes of air to water, and the rate of mass transfer. The relationship between these factors is illustrated in the following for a countercurrent flow packed tower, and then application to other air-stripping systems is discussed. Also of importance in design is the ultimate capacity of a system with respect to its ability to pass liquid and gas without flooding. This aspect is also briefly discussed in the following.

Countercurrent Packed Tower

Consider the countercurrent packed tower illustrated in Fig. 4. Air enters at the bottom of the tower and liquid at the top. The mass of volatile component $\underline{i}$ which is removed from the water must be contained in the air leaving the system. Thus, assuming the volume of the air and water streams do not change significantly during passage through the tower, and that the concentration of volatile component in the incoming air is zero,

$$Q(C_i^o - C_i^e) = GF_i^e \tag{13}$$

where,

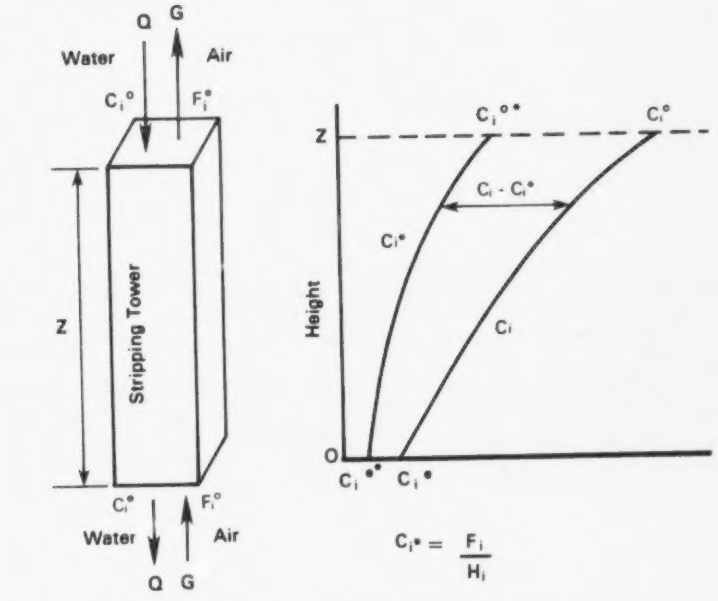


Figure 4. Flow scheme and concentration profiles for a countercurrent flow air stripping tower. Q and G represent water and air flow rate, and C_i and F_i represent concentration of volatile component i in the water and air, respectively. H_i is the Henry's law constant.

Q = water flow rate in m^3/s
G = air flow rate in m^3/s
C_i° = concentration of volatile component i in the influent water, mg/m^3
C_i^e = concentration of volatile component i in the effluent water, mg/m^3
F_i^e = concentration of volatile component i in the effluent air stream, mg/m^3

Then, the rate of removal of volatile component at any point within the tower is given by,

$$(Q/A)(dC_i/dz) = (K_l a)(C_i - C_i^*) \tag{14}$$

where C_i^* is the liquid concentration which is in equilibrium with the air phase concentration and equals F_i/H_i, and A is the tower cross-sectional area. The term ($C_i - C_i^*$) represents the driving force for removal of the volatile compound and varies throughout the column as illustrated in Fig. 4. The advantage of countercurrent operation is that C_i^* is high when C_i is high (at the liquid entrance to the tower) and C_i^* is low when C_i is low (at the liquid exit from the tower), thus maintaining a more uniform driving force throughout the tower. Higher air flow rates dilute the concentration F_i in the air phase and thus reduce C_i^*, increasing the driving force and the removal obtained. In order to determine the overall effect of these forces, Equation (14) can be integrated:

$$\int_0^z dz = (Q/A(K_La)) \int_{C_i^o}^{C_i^e} dC_i/(C_i - F_i/H_i) \qquad (15)$$

or in a short-hand form which is quite useful,

$$z = (HTU)(NTU) \qquad (16)$$

where, HTU equals the Q/A (K_La) portion of the right side of Equation (15) and is termed the height of a transfer unit, and NTU equals the value under the integral in Equation (15) and is termed the number of transfer units. An HTU is defined as the combination of flow and mass-transfer coefficient which gives one transfer unit of separation.

NTU is a term originated by Chilton and Colburn in 1935[17] and expresses the total change in bulk water concentration through the tower divided by the average effective driving force, $C_i - C_i^*$. In one transfer unit, the change in concentration just equals the effective driving force in that unit. An analytical solution for NTU for volatile components that obey Henry's law over the concentration range of interest is as follows[15]:

$$NTU = \frac{C_i^o - C_i^e}{(C_i - C_i^*)_{LM}} \qquad (17)$$

Here, the denominator represents the log mean of the driving force throughout the column and equals,

$$(C_i - C_i^*)_{LM} = \frac{(C_i^o - C_i^{o*}) - (C_i^e - C_i^{e*})}{\ln((C_i^o - C_i^{o*})/(C_i^e - C_i^{e*}))} \qquad (18)$$

General curves which relate removal efficiency and the height of a transfer unit to the number of transfer units are given in general references on separation processes[15,18,19]. As an example, the importance of a number of variables is illustrated in the following for removal of chloroform by decarbonators at Water Factory 21 in Orange County California[8]. The two decarbonators are countercurrent flow stripping towers designed for removal of carbon dioxide from this advanced wastewater treatment plant's reverse osmosis effluent, but have also been found to remove volatile organics as well. Each has a design flow Q of 0.11 m^3/s (2.5 mgd), is 2 m square and contains 2.4 m of polyethylene packing for a total volume per decarbonator of 9.6 m^3. A 5-horsepower (hp) blower on top of the decarbonator draws upward through the tower an air flow rate of 2.45 m^3/s at 50 mm of hydraulic head, or 22 m^3 of air per m^3 of water applied. Under these conditions, the measured removal efficiencies obtained for trihalomethanes are summarized in Table 2.

The values for NTU and HTU for the decarbonators can be determined by first solving Equation (13) for F_i^e, using the measured chloroform removal of 83 percent:

$$F_i^e = 0.11(10.6 - 0.17(10.6))/2.45 = 0.40 \text{ mg/m}^3$$

Table 2. Removal of Trihalomethanes by Countercurrent Flow Packed Tower Decarbonators at Water Factory 21

Trihalomethane	Influent Conc.* mg/m³	Percentage Removal	
		Mean	95% Conf. Inter.
Chloroform	10.4	79	70 - 85
Bromodichloromethane	4.1	85	76 - 91
Dibromochloromethane	1.7	71	49 - 84

*Geometric Mean

From Equation (1) and the value of H_c in Table 1,

$$C_l^{o*} = 0.40/0.141 = 2.83\ \mathrm{mg/m^3}$$

Equation (18) can then be solved to determine the average effective driving force for chloroform removal,

$$(C_l - C_l^*)_{LM} = \frac{(10.6 - 2.83) - (1 - 0.83)10.6}{\ln((10.6 - 2.83)/(1 - 0.83)(10.6))} = 4.09\ \mathrm{mg/m^3}$$

One transfer unit would thus remove 4.09 mg/m³ of chloroform from the bulk water. The number of transfer units in a decarbonator from Equation (17) is,

$$NTU = (10.6 - 0.17(10.6))/4.09 = 2.15$$

and the height of a transfer unit from Equation (16) is,

$$HTU = 2.4/2.15 = 1.12\ \mathrm{m}$$

The overall mass transfer coefficient can then be determined from $HTU = Q/A(K_La)$, thus

$$(K_La) = 0.11/(1.12)(4) = 0.0246\ \mathrm{sec^{-1}}$$

The above values can be used to answer questions about how the efficiency of chloroform removal would vary with the air to water (G/Q) ratio and with tower height, and what influence the Henry's law constant has on overall removal efficiency.

The effects of tower height and G/Q ratio on removal of chloroform are illustrated in Fig. 5. It was assumed here that Q/A remained constant so that K_La did not change. The curves illustrate that for chloroform little advantage in removal effi-

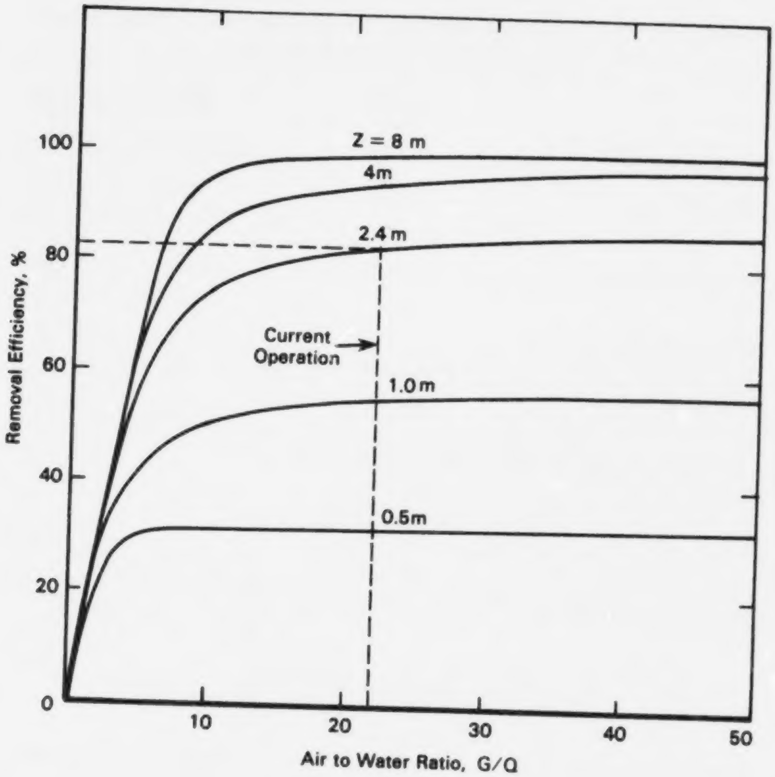


Figure 5. Computed effect of air to water (G/Q) ratio and tower height (z) on removal of chloroform by decarbonator with countercurrent flow. The water flow rate per unit cross-sectional area of tower is assumed constant.

ciency is obtained with G/Q ratios greater than about 20. At values above this, the concentration of chloroform in the effluent air stream is sufficiently low so that C_i^* approaches zero. The efficiency of removal is then essentially mass transfer limited, and changes in tower height are required to change removal efficiency. With G/Q ratios less than about five, however, increased tower height has little effect on removal efficiency. Here the rate of transfer is limited by the low air flow rate which provides insufficient dilution of chloroform to maintain a high driving force.

The effect of the Henry's law constant on removal efficiency by the Water Factory 21 decarbonators is illustrated in Fig. 6. For this case, the overall mass transfer coefficient (K_la) was assumed to be constant and equal to that for chloroform. For a given G/Q ratio, the higher the value of H_i, the higher the removal efficiency. Also, the higher the value of H_i, the lower the G/Q ratio at which the system becomes mass transfer limited. With the G/Q ratio of 22 used in the decarbonation tower at Water Factory 21, materials with an H_i value of 0.042 and above should be quite efficiently removed. From Table 1, this includes a large number of priority pollutants including chlorinated benzenes, several halogenated one- and two-carbon compounds, and several aromatic hydrocarbons. Another range of compounds with somewhat lower H_i values would be only partially removed, while several organic compounds including phenols and several pesticides would have almost zero removal.

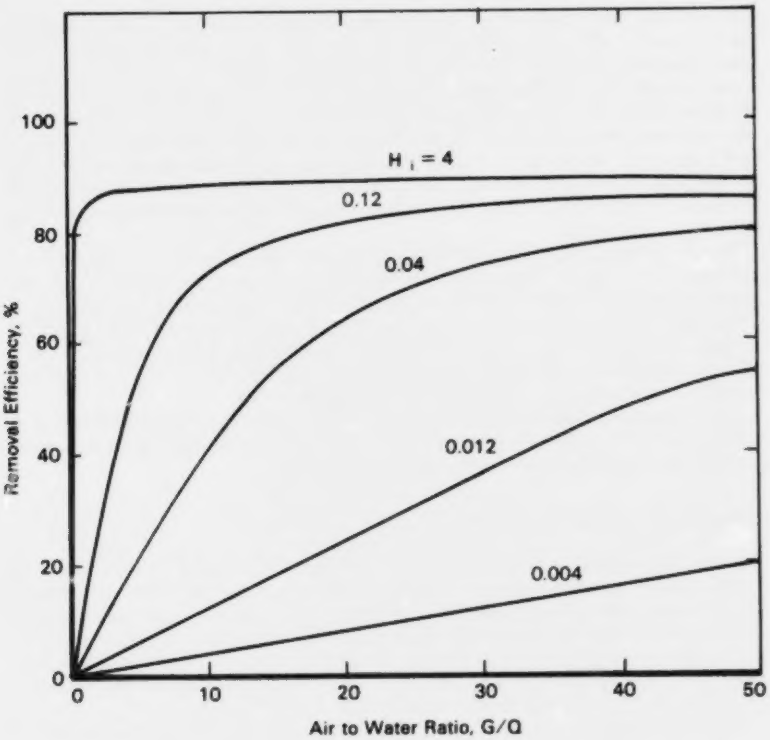


Figure 6. Computed effect of air to water ratio and Henry's law constant (H_i) on percentage removal for countercurrent flow stripping tower or decarbonator at Water Factory 21. The mass transfer coefficient is assumed constant and similar to that for chloroform.

Flooding

Flooding of a stripping tower results when the downward movement of water is prevented by the upward movement of air, and must be avoided. Flooding is related to the ability of the two phases to flow past each other in opposite directions in sufficient quantity and within the confines of the tower. The upward flow of air exerts a drag force on the falling water. This results in both an increase in pressure drop for the air and a reduced velocity of downward flow for the water. If the flows are increased, a point will be reached where the pressure drop for the rising air just equals the gravity head for the falling water which will then be unable to move through the packing at the desired rate; it will tend to build up in the tower and reduce the air flow rate. The tower then becomes unstable.

Countercurrent towers are generally designed to operate at no more than about 50 to 80 percent of their flooding limit in order to allow a factor of safety in the operation. Sherwood, et al.[20] developed a flooding correlation for packed towers, and these correlations have been modified by several researchers including Leva[21] and Peters and Timmerhaus[22]. These correlations are commonly given in reference texts[15,23] in the form of graphs relating gas and liquid flow rates, their physical properties, and the characteristics of the packing material.

From such correlations, Fig. 7 was prepared to illustrate the relationship between the G/Q ratio, the water application rate per unit, cross-sectional area of tower where flooding will occur $(Q/A)_f$, and the properties of the packing material. The figure was derived for randomly placed packing. With stacked packing, flooding occurs at higher flow rates. Design water flow rates should be about one-half of the $(Q/A)_f$ value obtained from the figure. The figure was also developed for air flow at one atmosphere of pressure. For operation at altitudes much above sea level, the actual G/Q ratio would need to be decreased in direct proportion to the decrease in atmospheric pressure to obtain the proper value for the abscissa of the graph in Fig. 7.

The F values or packing factors are related to the properties of the packing material, with typical values given in Table 3. The lower the packing factor, the higher the capacity of the tower as indicated in Fig. 7. Low packing factors are associated with low packing surface areas per unit volume of tower and with high void volume in the packing material. The factors which tend to make F low also tend to decrease the overall rate of mass transfer so that a compromise between these factors is necessary in selecting an appropriate packing material.

Fig. 7 shows that with higher G/Q ratios, the liquid loading where flooding occurs is reduced. Thus, higher air flow not only requires larger power requirements and larger fans, but also larger tower cross-sectional area.

Cross-Flow Stripping Tower

Cross-flow stripping towers are used extensively for water cooling at chemical plants and power plants, and also for ammonia stripping at wastewater treatment plants because they permit a high air flow rate with respect to water flow rate with relatively small energy usage and without flooding. They also offer promise for removal from water of more soluble trace organic compounds, or those with a relatively low Henry's law constant. The relationship between air and water flow in a cross-flow stripping tower is illustrated in Fig. 8.

Higher air flow rates are possible with cross-flow towers because the side area of the tower through which the air flows is relatively large and thus the air flow rate per unit of area is small. The disadvantage is that the efficiency of contaminant removal for a given air to water ratio is less than in a counter-current packed tower. As air flows horizontally through the tower, a volatile contaminant is stripped from the water which flows downward through the packing. The contaminant concentration in the air leaving the tower is higher than in that entering the tower, and so the driving force for removal is less on the leaving side. Therefore, as illustrated in Fig. 8, the concentration profile for the volatile compound in the water on the two sides of the tower, and at any point in between, is different.

Thibodeaux, et al.[24] have recently developed an analytical solution for volatile compound removal by cross-flow towers which is similar to the number of transfer unit approach described in the previous section for counter-current flow towers. The reader is referred to their article for details. Their approach was taken to analyze the operation of the large cross-flow stripping towers used at Water Factory 21 for removal of ammonia from reclaimed wastewater. In this analysis, the efficiency of ammonia removal measured was used to estimate the overall mass transfer coefficient for the tower, and with this value in hand, the efficiency that should be obtained as a function of air to water ratio and Henry's law constant was calculated.

The polypropylene splash-bar packing over which water cascades in each of the two Water Factory 21 ammonia stripping towers is 55 m long by 4.9 m wide and 7.3 m deep for a total volume per tower of 1970 m^3. The packing consists of 1.3 cm diameter bars spaced 7.6 cm apart in crisscross pattern for alternate rows. Air is drawn horizontally through the packing by six 125-hp fans, each 5.5 m in diameter. The fans are operated by 2-speed electric motors which can draw 990 m^3/s through each tower, or 3000 m^3 air per m^3 of water at the design water flow rate of 0.66 m^3/s.

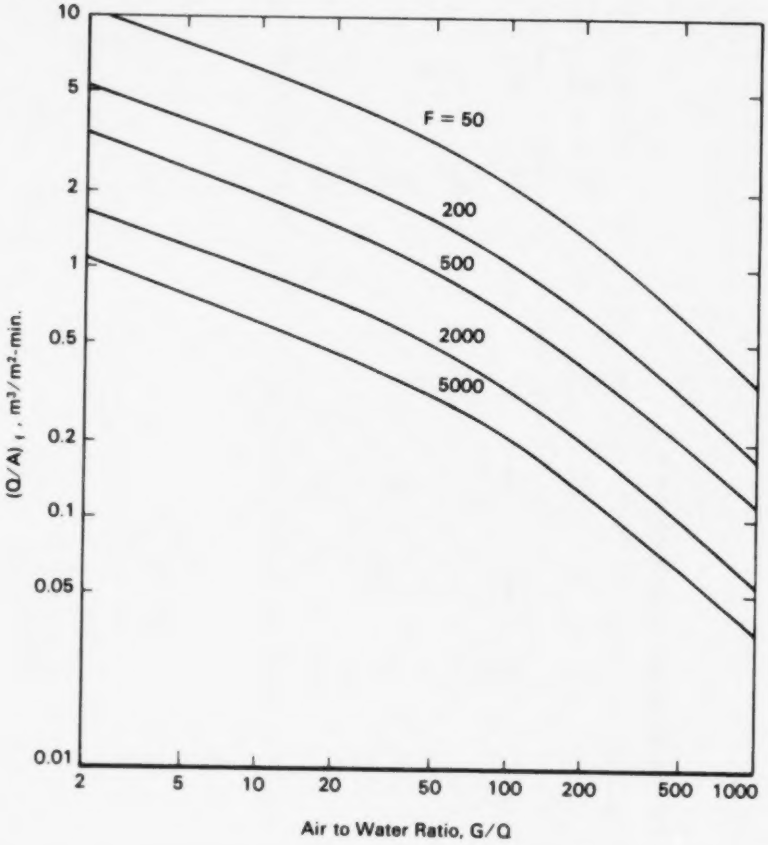


Figure 7. Relationship between the air to water ratio (G/Q) and the water flow rate per unit cross-sectioned area of tower $(Q/A)_f$ which produces flooding in countercurrent flow towers for packing media with various F values.

The pH of the water applied to the stripping towers was generally about 11.2 as required for efficient ammonia removal. However, for the volatile organic compounds studied, removal efficiency should be independent of water pH.

The influent and effluent concentrations to the tower for ammonia and a range of trace organic compounds as determined for two of the three different periods of Water Factory 21 operation are listed in Table 4. Also listed are the average percentage removal and 95 percent confidence intervals for the average removals[6]. During the second period covering a year and one-half of operation, Water Factory 21 received a trickling filter treated wastewater which had a high ammonia and volatile organic concentration, and the fans were in full operation. However, during the third period covering about nine months of operation a nitrified activated sludge effluent was treated and the fans were not operated as ammonia removal was not necessary. However, some removal of ammonia occurred and a high percentage removal of several volatile trace organic compounds was also still obtained. Air movement then occurred through the tower by natural draft even though the fans were not in operation.

Table 3. Packing Factors F for a Variety of Packing Materials (After Nonhebel[18])

Nominal Packing Size (mm)		6	13	16	19	25	32	38	51	76
Type of Packing	Material	Packing Factor-F								
Raschig rings	Ceramic	4590	2100	1250	855	525	410	310	215	120
0.8 mm wall	Metal	2300	985	625	510	375	-	-	-	-
1.6 mm wall	Metal	-	1115	950	755	475	360	270	185	105
3.0 mm wall	Metal	-	-	-	-	-	-	-	-	125
Berl saddles	Ceramic	2950	785	-	555	360	-	215	150	-
Intalox saddles	Ceramic	1970	655	-	475	320	-	170	130	-
Pall rings	Plastic	-	-	320	-	170	-	105	82	-
Pall rings	Metal	-	-	235	-	155	-	92	66	-

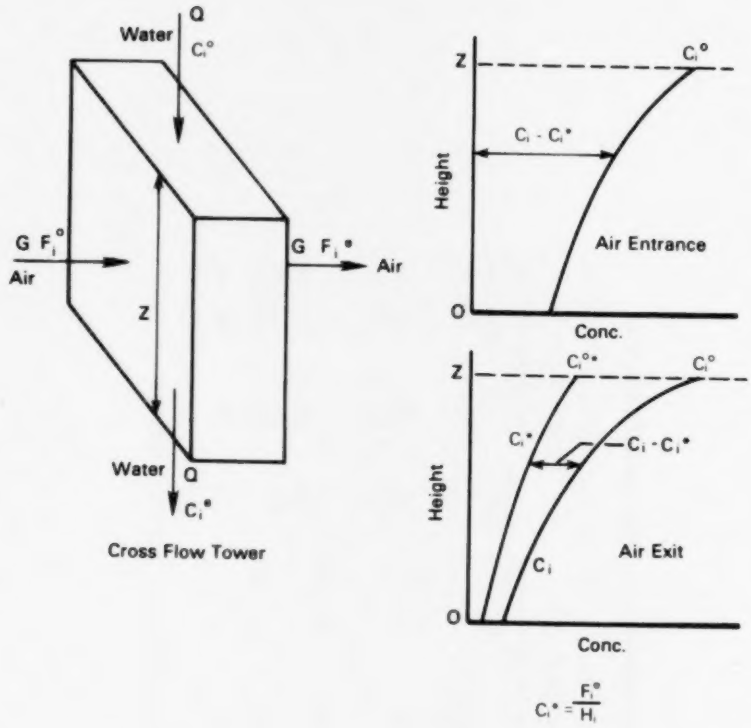


Figure 8. Flow scheme and concentration profiles for a cross flow air stripping tower. For air entrance concentration profile, F_i° assumed equal to zero.

The overall mass transfer coefficient for ammonia removal during the second period as defined by Thibodeaux, et al.[24] was found to be 0.0009 $\sec^{-1}$, and using this value and their procedure, the efficiency of ammonia removal was found as a function of the air to water ratio. First, the air flow rate was assumed constant at 990 m^3/s for each tower and the water flow rate was assumed to vary. Since H_i for ammonia is low, the transfer is predominantly gas-phase controlled, and with constant gas flow rate the overall mass transfer coefficient should not vary. Next, the water flow rate was held constant at 0.66 m^3/s and the air flow rate was allowed to vary. For this case the mass transfer coefficient would be a function of the air flow rate and was assumed to equal $5.43\,(G/990)^{0.64}$ as cited in the literature[24]. The results for both the water variable and air variable cases are shown in Fig. 9. The difference between the two cases is not great. One might use these results to estimate the air flow rate during the third period when the fans were not in operation. For 25 percent ammonia removal the air to water ratio should be 225, or the range based upon the 95 percent confidence interval of removal, the ratio would range from 100 to 350. These values correspond to gas flow rates per tower of 150 with a confidence interval range of 66 to 230 m^3/s.

The air to water ratios obtainable for the ammonia stripping towers are quite high, and should be sufficient to remove a wide range of volatile organic compounds. Assuming the liquid-phase controlled mass-transfer coefficient for ammonia applied,

Table 4. Removal of Volatile Compounds by Cross-Flow Packed Stripping Tower at Water Factory 21

	Fans Operating			No Fans Operating		
		Percentage Removal			Percentage Removal	
Compound	Influent Conc.* mg/m³	Mean	95% Conf. Interval	Influent Conc.* mg/m³	Mean	95% Conf. Interval
Trihalomethanes						
Chloroform	1.1	83	70 - 91	4.1	79	64 - 87
Dibromochloromethane				0.8	82	76 - 87
Chlorobenzenes						
Chlorobenzene	3.0	96	88 - 99			
1,2-Dichlorobenzene				0.6	88	61 - 96
1,3-Dichlorobenzene				0.1	83	60 - 93
1,4-Dichlorobenzene	1.0	97	88 - 99	1.3	92	89 - 94
Tetrachloroethylene				2.5	95	88 - 98
1,1,1-Trichloroethane				4.7	91	76 - 96

*Geometric Mean

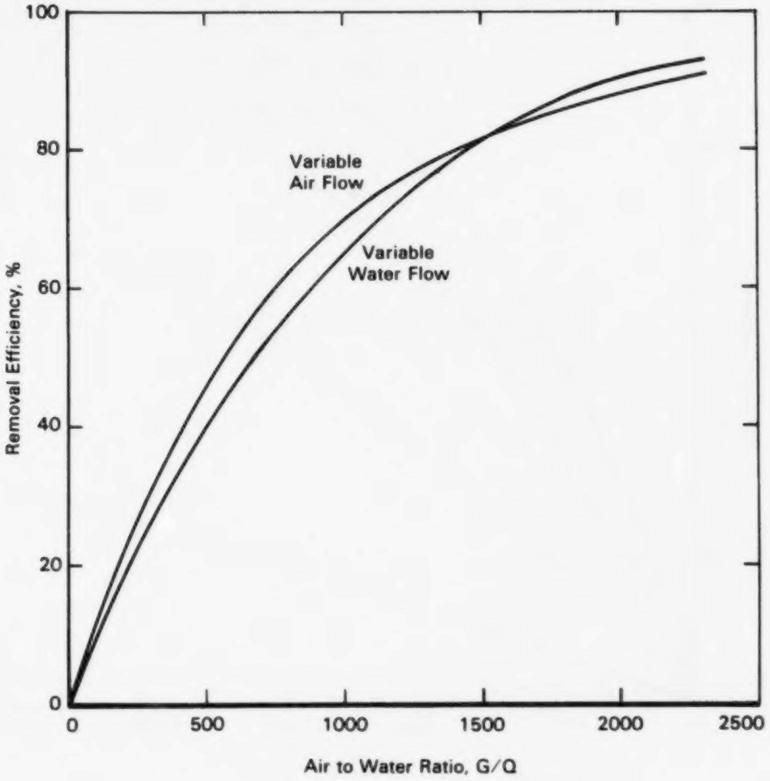


Figure 9. Calculated effect of air to water ratio (G/Q) on efficiency of ammonia removed by Water Factory 21 cross-flow stripping tower. In one case, the G/Q was changed by varying the air flow rate, and in the other case by varying the water flow rate.

percentage removals of volatile materials as a function of air to water ratio and Henry's law constants were calculated. The results are shown graphically in Fig. 10. Compounds with Henry's law constants down to almost 10^{-3} should be efficiently removed by the cross-flow stripping towers. Based upon the compilation in Table I, this represents a large number of priority pollutants. Unfortunately, adequate data were not obtained for removals of compounds other than those with relatively high H_i values, and so the true potential of cross-flow towers was not measured. In fact, most compounds for which adequate data were obtained could be removed well by the normal counter-current stripping towers. They were all removed efficiently by the ammonia stripping tower, even when the blowers were not in operation. The latter indicates that natural-draft towers may have potential for stripping of relatively volatile compounds and at low energy consumption. The trade-off is higher capital cost for tower construction.

Clearly, cross-flow stripping towers have good potential for removal of organic compounds with intermediate water solubility and Henry's law constants. Also, if designed for natural draft rather than forced draft, they may offer potential for removal of more volatile compounds at low energy cost. These areas deserve further study.

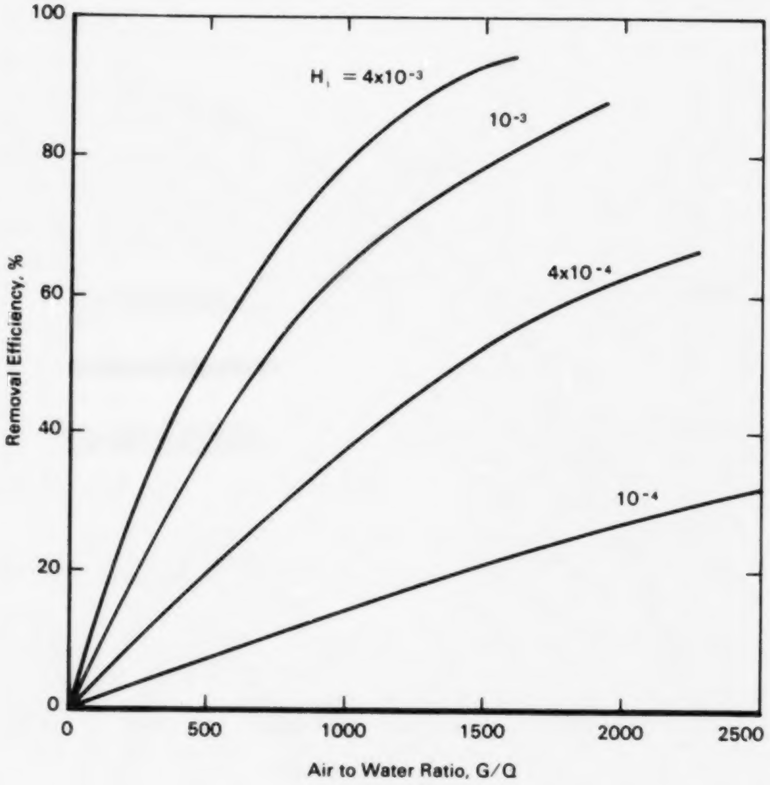


Figure 10. Calculated effect of air to water ratio and Henry's law constant on removal efficiency by Water Factory 21 cross-flow stripping tower.

Stripping Basins

In stripping basins for removal of organic contaminants, air is brought into contact with water either by diffused aeration or mechanical aeration. Such basins are commonly used for introducing oxygen into biological treatment systems, and experience developed on mass transport rates for oxygen are directly applicable to the design of stripping basins.

Fig. 11 illustrates the flow of air, water, and volatile material in diffused aeration and mechanical aeration stripping basins. The air and water flow rates are easily monitored in a diffused aeration system, and so control of the air to water ratio is relatively straightforward. In a mechanical aeration system, however, the air flow is generally not controlled and varies randomly with such factors as wind speed. This problem was considered at a mechanical aeration stripping basin designed for the Palo Alto, California, wastewater reclamation plant operated by the Santa Clara Valley Water District. Here blowers were installed to draw air across the basin in an effort to enhance the removal of ammonia from the wastewater. This system is used as an example in the following to illustrate the variables of importance in a stripping

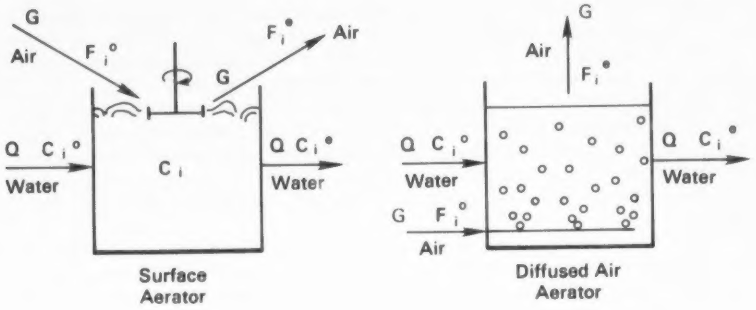


Figure 11. Flow schemes for surface aerator and diffused air-stripping basins.

basin. Diffused aeration systems behave in a similar fashion and so the analysis is appropriate for their design also.

For this analysis it is assumed that the mechanical aerator results in the complete mixing of the basin contents so that the concentration of volatile compound C_i is the same throughout the basin. For this case the effluent concentration of the compound C_i would also equal the basin concentration. Also, it is considered that the air being drawn over the top of the basin contains none of the compound so that F_i^o equals zero. The air is also considered to be completely mixed over the top of the basin by the mechanical aerator so that the concentration there and indeed in the air leaving the basin is the same and equals F_i^e. For this case under steady-state conditions of operation, the difference between the mass flow rate of volatile component flowing into the basin and flowing out of the basin equals that leaving the basin by stripping, or

$$Q(C_i^o - C_i^e) = K_i a V(C_i^e - C_i^*) \tag{19}$$

where V is the basin volume in m^3. Since the volatile compound enters the air, then it must also be true that

$$GF_i^e = K_i a V(C_i^e - C_i^*) \tag{20}$$

The value C_i^* represents the water concentration of compound i which is in equilibrium with the air concentration and from Equation (1) equals F_i^e/H_i. By combining this relationship with Equations (19) and (20) and rearranging, the following equation for the fractional removal of compound i through mechanical aeration basin stripping results

$$\frac{C_i^o - C_i^e}{C_i^o} = \frac{1}{1 + \frac{Q}{VK_i a} + \frac{Q}{GH_i}} \tag{21}$$

Equation (21) was used to evaluate the stripping basin at the Palo Alto reclamation plant. This basin treats a steady flow of 0.044 m^3/s (1 mgd) and is 16.8 m long, 9.1 m wide, and 5.8 m deep for a total volume V of 887 m^3. The basin contains two 50-hp floating spray mechanical aerators. A 30-hp centrifugal fan draws 19 m^3/s of air under 3.8 cm of static pressure through a series of 0.3 m × 0.6 m openings located just above the basin water surface causing air to flow down and over the basin. Grab samples were collected of the basin influent and effluent once per week over a period of about two months and analyzed for removals obtained for several volatile organic compounds. The results are summarized in Table 5. Removals in general were above 90 percent.

Equation (21) was rearranged and used to calculate the mass transfer coefficient for the measured chloroform removal, giving a value for K_la of 0.0007 per sec., with a range based upon the 95 percent confidence interval for removal of 0.0003 to 0.002 per sec. Values within this range were also obtained for the chlorinated benzenes, but for the chlorinated ethanes and ethylenes, the average values were all near the upper end of the range. The reason for the higher values for the latter needs further exploration.

It is common in the design of mechanical aeration systems to specify transfer efficiencies in mass of a compound transferred per unit time per unit of energy input to the aerator under some standard operating conditions. For example oxygen transfer ratings are commonly expressed in pounds per hour per unit horsepower. Through introduction of appropriate conversion factors such values can be converted to give mg transferred per m^3 of basin per second (r) as follows:

$$r = 0.126m/V \tag{22}$$

where 0.126 converts lb/hr to g/s, and m is the aerator rating in lb/hp-hr under standard conditions. For oxygen the standard conditions are generally 20°C, for which the saturation concentration for oxygen at one atm is 9.2 g/m^3 and the basin dissolved oxygen content is zero. The mass transfer coefficient would then be

$$K_la = 0.126mP/V(9.2 - 0) \tag{23}$$

where P is the horsepower rating for the blower. The value for m is not known for the mechanical aerators at Palo Alto, but typical values are 2 to 4 lb/hp-hr. This would give a range of computed K_la values from 0.003 to 0.006/s. From Equation (8) and diffusion coefficients in Table 1, the value for chloroform should be about one-half of that for oxygen. While the data available are not adequate to provide a good test, the K_la value obtained for chloroform appears in the correct range. Equation (21) indicates that both the detention time of water in the basin (V/Q) and the air to water ratio (G/Q) affect the fractional removal of a volatile component. Using the mass transfer coefficient determined for chloroform, the effect of these variables was determined for the Palo Alto stripping basin, and the results are illustrated in Fig. 12. The air flow rate used is obviously much higher than needed to remove chloroform efficiently. Also, the detention time could be lowered significantly with little effect on removal, although the present basin is about what is required to adequately handle the mechanical aerators. The selection of optimum operating conditions for a desired removal efficiency should consider construction and operating costs. The biggest factor in the operating costs are for power to operate the aerators and the blower.

An analysis of a diffused air system is not given here because of space limitations, but would be similar to that given for the mechanical aeration system. In a similar way, experience with oxygen transfer by diffused air systems should be most helpful in design. A limitation is that power requirements for introducing air under a high

Table 5. Removal of Organic Compounds by Spray Aeration Stripping Basins at Palo Alto Wastewater Reclamation Plant

Compound	Number of Paired Samples Analyzed	Influent Conc. mg/m³	Percentage Removal Mean	Percentage Removal 95% Conf. Interval
Total Chlorinated Organics				
Purgeable	5	168	95	91 - 98
Non-purgeable	5	151	5	-28 - 30
Chloroform	6	18	92	84 - 96
Bromodichloromethane	6	1.9	94	84 - 98
Dibromochloromethane	6	0.50	82	31 - 95
1,1,1-Trichloroethylene	6	106	99	97 - 99.7
Trichloroethylene	6	38	99	97 - 99.6
Tetrachloroethylene	6	58	99	98 - 99.8
1,2-Dichlorobenzene	5	8.3	91	68 - 97
1,3-Dichlorobenzene	5	3.1	94	80 - 98
1,4-Dichlorobenzene	5	5.1	92	76 - 97
1,2,4-Trichlorobenzene	5	14	92	79 - 95
Octylcyanide	5	0.97	86	49 - 96
Nonylcyanide	5	0.25	70	33 - 86

hydrostatic pressure is much greater than for a mechanical aeration system, and so diffused aeration could be quite expensive if a high air to water ratio were required. They may, however, be more economical for removal of more volatile compounds where high G/Q ratios are not required.

SUMMARY AND DISCUSSION

Many different methods are available for stripping volatile organic materials from water, but in general they rely upon the same physical principles. The major characteristic of organic compounds affecting the ease with which they can be removed from water is Henry's law constant, the higher the value, the more volatile the compound and the more readily it can be removed from water. The rate of mass transfer of a compound from water is also a function of its diffusivity, but this characteristic does not vary greatly within the range of organic compounds which are susceptible to stripping.

The three major factors that affect the efficiency of removal by a given process are the air to water ratio, the detention time, and the rate of mass transfer. In a stripping tower the actual detention time of the water is not readily measured, but is a function of the tower height which is generally the design variable used. For a given system with a given rate of mass transfer, less volatile compounds require either a greater detention time in which to accomplish a given efficiency of removal, or a greater air to water ratio in order to increase the driving force for the transfer. Mass transfer may be either liquid-phase controlled for compounds with Henry's law constants well above 7×10^{-3}, or gas phase controlled when values are well below this. When removals are liquid-phase controlled, then mass transfer coefficients determined

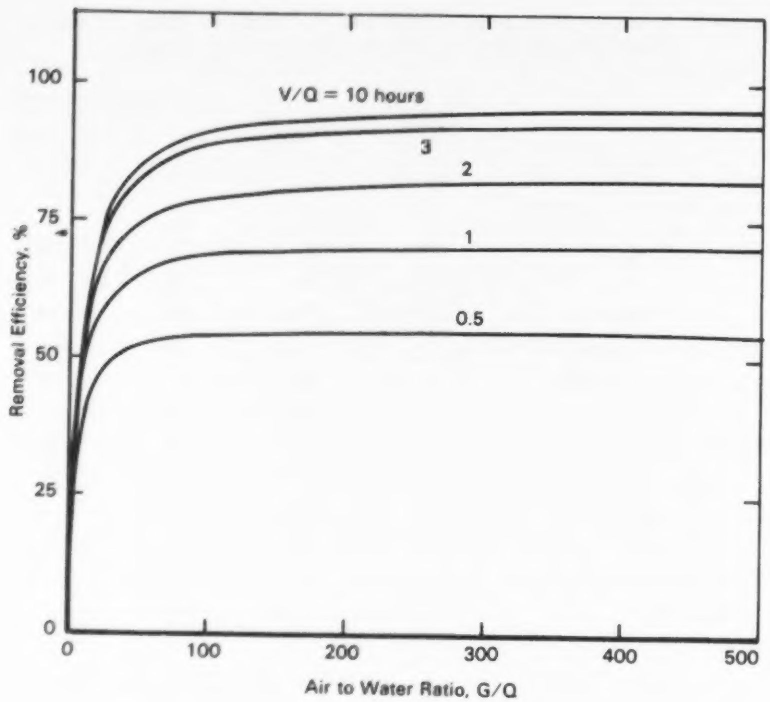


Figure 12. Computed effect of air to water ratio (G/Q) and water detention time (V/Q) on chloroform removal by the Palo Alto Reclamation plant mechanical aerator stripping basin.

with oxygen can be used for design after appropriate correction for differences in diffusivity are made. When removals are gas phase controlled, then transfer coefficients for other materials such as ammonia can be used. The mass transfer coefficient for a given system is a function of many factors, but in general the greater the turbulence of the controlling phase and the greater the exposed air-water surface, the higher the rate of transfer.

Finally, the most appropriate system for a given situation depends upon economics plus a variety of other considerations previously mentioned. Perhaps the major trade-off is between construction cost and power costs. Table 6 presents a summary of the power requirements and system volume for the two tower strippers and the mechanical aeration stripper discussed in this chapter. Also included is an estimate of power requirements for a diffused air system. It is obvious that for high air to water ratios, stripping towers or a mechanical aeration system with air flow across the basin are far superior to a diffused air system. Also, in order to achieve very high air to water ratios without flooding, cross-flow towers have a decided advantage over counter-current towers.

Experience is relatively limited with the use of stripping towers for removing hazardous organic chemicals from water supplies. In this chapter an attempt was made to illustrate that the fundamental principles of strippers have been quite well developed within the chemical engineering field and are directly applicable to the water treatment field. One need is for a good economic analysis of the different

Table 6. Summary of Operational Characteristics and Power Requirements for Various Stripping Processes

	Operational Characteristics					Horsepower Requirements			Horsepower per m³/min. of flow	
Process	Volume m³	Q m³/s	G/Q	V/Q min.	$K_l a$ sec⁻¹	Hydraulic Head Pumping*	Mech. Aerator	Blower	Water †	Air‡
Countercurrent tower (decarbonator)	9.6	0.11	22	1.45	0.025	8.4	0	5	1.3	0.034
Cross flow tower (ammonia stripping)	1970	0.33	2700	99	0.0009	61	0	750	3.1	0.014
Mechanical aeration (ammonia stripping)	887	0.044	430	336	0.007	0	100	30	38	0.026
Diffused aeration										1.5§

*Assumed 60% overall efficiency for pumping.

†Hydraulic head or mechanical aerator power requirements divided by Q expressed in m³/min.

‡Blower horsepower divided by air flow rate in m³/min.

§Calculated using Eq. 12.9, p. 510, Metcalf and Eddy, *Wastewater Engineering*, McGraw-Hill (1972), for blower brake horsepower, 70% power efficiency, 30°C ambient temp, and 8 psi discharge pressure.

stripping processes in order to determine more precisely when each is most appropriate for use. Another concern is that stripping processes result in the transfer of a contaminant from one media to another, and since the overall objective of treatment is to reduce human exposure one must be certain that stripping does not simply substitute one problem for another. In this vein, research is needed to evaluate methods for cleaning the air of the volatile compounds after removal from water. Perhaps activated carbon can be used for this purpose. An advantage might be that the carbon would be spent less rapidly than if used directly with water, and regeneration costs could be greatly reduced. Additional research is also needed to evaluate the effectiveness of air-stripping for removal of less volatile compounds. While two of the stripping processes discussed in this chapter had adequate air to water ratios to accomplish this, adequate analyses were not available to evaluate removals for compounds with lower Henry's law constants. Research is also needed to better evaluate the Henry's law constants and diffusivity for compounds of importance since the values presented here are simply unverified estimates.

In summary, air-stripping has good potential as an economical water treatment process. It has a long history of usage in the water treatment field for removal of inorganic gases and some taste and odor producing compounds, and has direct relevance to the organic problems of concern today. It has potential for direct treatment of surface waters that may contain many different volatile organic chemicals, for disinfected waters containing high concentrations of trihalomethanes, and for contaminated groundwaters that in a growing number of cases contain volatile organic chemicals in relatively high concentration. Today, there appears to be many new and important applications for this old water treatment process.

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OXIDATION OF ORGANIC SUBSTANCES IN DRINKING WATER

William H. Glaze

INTRODUCTION

Although oxidation processes occur to some extent in virtually all drinking water treatment plants, oxidation per se has not been viewed traditionally as an important unit process. Two classic texts on water treatment by Hopkins and Bean[1] and by James[2] do not list oxidation as a principal method for drinking water treatment. Several decades after the original appearance of these texts, two newer monographs by Culp and Culp[3] and Hammer[4] also do not list oxidation techniques in their chapter headings. Two reference texts on water treatment by the Nalco Chemical Company[5] and Degremont[6] cover oxidation-reduction processes, but the emphasis in the drinking water sections is on disinfection. No discussion of the use of oxidants for control of toxic organic substances is given. In a recent two volume review on water reuse and recycling technology by the firm of Culp/Wesner/Culp,[7] removal of organic substances is covered briefly with no mention of oxidation as an alternative treatment method. Ozonation is covered only in a section emphasizing its disinfection capability.

This situation most surely will change in the coming decade as more stringent standards for drinking water quality are prescribed.[8] In particular, oxidation processes offer one of the few means for the removal of potentially toxic organic substances such as pesticides, industrial solvents, and other synthetic organic chemicals. These substances generally are not removed by traditional water treatment processes, and to the extent that their presence is a source of concern, oxidation processes may develop into important treatment alternatives.

When speaking of oxidation processes in drinking water treatment, most authors confine their discussion to iron and manganese control and to the destruction of offensive tastes and odors.[1-4] While some citations to these applications will be listed, this review will discuss mainly the use of oxidants for control of synthetic organic chemicals. We also shall include in our discussion the oxidation of naturally occurring organic compounds (such as trihalomethane precursors) which may be transformed by disinfection processes into by-products of concern to human health.

Three oxidation processes will be emphasized in this chapter: chlorine (in its various aqueous forms), ozone, and chlorine dioxide. In addition, other oxidants such as permanganate, hydrogen peroxide and catalytic systems such as ozone with ultraviolet radiation will be discussed. In most cases, the oxidation process will be discussed in terms of its basic chemistry, studies which reveal its relative efficacy for organic compound removal, and the expected costs of applying the process to water treatment. Evidence concerning by-product formation will also be presented.

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Basic Discussion of Oxidation Processes

Although one usually thinks of oxidation as a chemical reaction involving oxygen such as the burning of a fuel, literally speaking, oxidation refers to the loss of electrons by the substance being oxidized.[9] This process need not involve oxygen; for example, it may happen at an electrode in an electrolysis cell. In water treatment applications, however, oxidizing agents usually involve an active chemical species which contains oxygen.

Oxidation always involves the increase in the oxidation state of the oxidized species; for example, when carbon monoxide is oxidized to carbon dioxide (Equation 1),

$$2CO + O_2 \rightarrow 2CO_2 \qquad (1)$$

the formal oxidation state of carbon increases from the +2 state to the +4 state. Simultaneously, and by necessity, the oxidizing agent (oxygen in this case) is reduced to a lower oxidation state. Water treatment oxidants may involve oxygen as the reducible species, as in ozone, hydrogen peroxide or oxygen itself. Alternately, another element may be reduced (i.e., act as the oxidant) as manganese in MnO_4^- or chlorine in chlorine dioxide or hypochlorite.

All of these oxidants have sufficient oxidizing power to oxidize organic compounds to carbon dioxide. This power is measured by the standard potential (E°) of the agent acting as one-half of a redox cell. Values of E° are listed in Table I for six important oxidants.[10] By convention, the reactions are written as reduction processes.

One may use these thermodynamic potentials to calculate the overall free energy change of a redox process in order to establish whether the process should be spontaneous. For example, reactions (2) through (4) describe the permanganate oxidation of oxalic acid, a relatively refractory compound.

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O \qquad (2)$$

$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^- \qquad (3)$$

$$2MnO_4^- + 3H_2C_2O_4 + 2H^+ \rightarrow 2MnO_2(s) + 4H_2O + 6CO_2 \qquad (4)$$

E° for the net reaction (4) is calculated from the sum of E° values in Table I for the half reactions. The value is 2.19 volts and the free energy change, −303 kilocalories, is calculated from $-nFE^\circ$ where n is the total electrons (six) transferred in Equation (4) and F is the Faraday constant. The high negative free energy change shows that reaction (4) should occur spontaneously.[11] In actual fact, the process, while thermodynamically allowed, is too slow for application in a real water treatment situation. This situation prevails for most organic oxidation processes. Although oxidation of substrate may occur, the product usually is not carbon dioxide; rather, a series of partially oxidized by-products are formed. In short, few oxidation processes even as simple as Equation (4) occur as predicted by thermodynamics. They must be tested in actual reaction systems to determine their feasibility. In the case of the oxidants considered here, all are theoretically capable of oxidizing organic substances to CO_2, but in actual practice, conditions are seldom extreme enough to reach this goal and the oxidation process is usually incomplete.

It is interesting to note that this conclusion does not apply to many biological systems, where oxidation to carbon dioxide is accomplished routinely.[12] Indeed many life processes consist of the oxidation of carbonaceous substances as a means

Table 1. Potentials of Selected Oxidants at 298°K[10]

Half-Reaction	E° (Volts)
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O$	1.70
$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$	1.51*
$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	-0.49

*Value calculated since couple is unknown.

of deriving energy for the sustenance and reproduction of the species. The biological degradation of organics in wastewater treatment is merely an exploitation of these processes for purification purposes. Lately there has been much renewed interest in the utilization of biological oxidation for the removal of organic impurities from drinking water. Particular attention is being focused on bacterial oxidations which may occur on filters, especially granular carbon filters.[13-14] We shall return to that subject in a later section of this chapter.

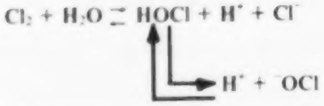
Not all organic compounds are biodegradable, of course. Carbon in nature often occurs in highly reduced states such as coal, peat and petroleum hydrocarbons which cannot easily be assimilated by biochemical systems. Moreover, it is very common for organic substances of ecological concern to be in a reduced state. Polynuclear aromatic hydrocarbons, most pesticides and other synthetic organic chemicals thus are candidates for oxidation. Because these substances are non-polar, they may accumulate in lipid tissues.[15] As they are oxidized, they become more water soluble and generally more biodegradable.[16] However, they are not necessarily less toxic in these intermediately oxidized forms, as the metabolites of benzo[a]pyrene attest.[17] In this case, it is the oxygenated metabolites, not the original compound, which have been identified as active carcinogens.

The implications of all of these considerations are often missed by scientists and engineers who propose to utilize oxidation processes for removal of toxic substances in drinking water. Such processes seldom remove the organic matter; they merely convert it to a set of new by-products of intermediate oxidation states. While the toxicity due to the original substrate may be removed in the process, other toxic effects may be substituted due to the formation of by-products. Viewed in this light, by-product studies become a necessary and important part of R & D programs which evaluate oxidizing agents. EPA studies directed toward this goal are presently in progress.

Finally, it should be noted that oxidation processes are often energy intensive and costly unit processes which may add significantly to the cost of water treatment.[18] To a large extent this explains the lack of common use of these processes in present treatment plants. Oxidation with permanganate or other chemicals is now used only as a last resort when other cheaper methods fail, as in taste and odor crises. Nonetheless, with the advent of concern over synthetic organic chemicals in drinking water, and with the increase of interest in water reuse, chemical oxidation processes are subjects of several recent research and demonstration projects. One may expect this interest to continue as criteria for water quality grow more stringent.

CHLORINATION AS AN OXIDATION PROCESS

Chlorination has been used in drinking water treatment since before the turn of the century, primarily as a disinfectant.[19] White has reviewed the chemistry of aqueous chlorine[20] and has pointed out it is hypochlorite ion (^-OCl) and hypochlorous acid (HOCl) which under usual conditions are the principle chemical species (Equation 5). The former predominates at high pH, the latter at low pH with the transition occurring near pH 7.5.

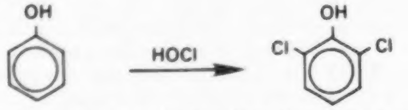


$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad HOCl \rightleftharpoons H^+ + {}^-OCl$$

(5)

Both of these species are strong oxidizing agents, having standard electrode potentials of 1.49 and 0.90 volts, respectively (Table 1). Even when used as a disinfectant, chlorine acts also as an oxidizing agent of organic material in the water.[21] Indeed most authorities in the field suggest that the majority of the chlorine demand* in drinking water treatment is due to oxidation processes.[22]

Chlorine in its aqueous forms has another chemical property which has become of paramount importance in recent years--the ability to substitute for hydrogen in certain organic chemical environments.[24] It is this property which leads to the formation of carbon-bound chlorine during drinking water disinfection. This fact was first appreciated by workers concerned with phenolic tastes and odors who showed that chlorophenols are produced from chlorine and phenol.[25] Reaction (6) symbolizes this process.



(6)

The product 2,6-dichlorophenol has often been identified as one of the principal compounds of bad taste produced by chlorination of waters containing phenol.[26]

More recently it has been shown that chlorination of waters containing natural organic materials produces a series of organohalides as complex as the natural matrix which is their precursor.[27-29] Most infamous of these are the trihalomethanes, $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ first discovered by Rook of the Netherlands early in the past decade.[27] These four substances are produced by the chlorination of natural organics in water by a still unknown process, partly reflecting our ignorance of the nature of aquatic humus.[30] Work on the trihalomethane question in the United States has centered in Cincinnati, Ohio, at the U.S. Environmental Protection Agency (EPA) Environmental Monitoring and Support Laboratory (EMSL) where Bellar, et al. discovered THMs in drinking water almost simultaneously with Rook.[31] A detailed discussion of the chemistry of this subject is beyond the scope of this chapter. We shall note simply that THMs are produced by the reaction sequence (7) to (8), where the term "precursor" refers to the unidentified constituents of natural water which lead to THMs upon reaction with chlorine.[32]

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{7}$$

$$\text{HOX + Precursors} \rightarrow \text{THMs + Other Oxidized and Halogenated Organics} \tag{8}$$

---

*Chlorine demand is defined as the amount of chlorine dose (in mg/L) required to just form a free hypochlorite residual in a given water source.[23]

Note that natural bromide in the water is responsible for brominated THMs which may predominate in highly saline water.[33] Also note that other chlorinated by-products are produced in this process. Fig. 1 is taken from an EPA-sponsored study in which several treatment options for organics control are being investigated.[34] The figure shows total trihalomethane (TTHM) and total organic halogen (TOX) values obtained by laboratory chlorination of samples taken from a surface water in the southern USA. These and other recent studies have shown that the amount of chlorine bound in the form of volatiles other than THMs and non-volatile organic by-products may exceed THM concentrations by a factor of two to five.[35] The nature of these by-products and their effects on human health are unknown at this time.

Equation (8) also shows that oxidized organic compounds are produced by the chlorination process. In one system with a DOC level of 8.4 mg/L, a dose of chlorine of 20.0 mg/L leaves a free residual of hypochlorite of 0.6 mg/L (as Cl) after 72 hours contact time; thus, the chlorine demand was 19.4 mg/L (as Cl). The THM yield was 257 μg/L (as Cl), and the yield of other organic halides was 976 μg/L (as Cl).[36] The demand for oxidation reactions is calculated as follows:

$$(20.0 - 0.6 - .257 - 0.976) \simeq 18.2 \text{ mg/L}$$

In other words, 91% of the chlorine expended in the reaction acts as an oxidizing agent and presumably ends up as chloride ion (Cl^-). This is not an unusual figure and it symbolizes the oft-forgotten fact that chlorine in water treatment acts mostly as an oxidant. Chlorinated by-products, particularly the THMs are produced in very low yields (6% in the case above). This is not to imply, of course, that the yields are insignificant as the impact of recent legislation attests.[8] Indeed, it is the need to minimize THM levels in finished drinking water that has stimulated much of the recent research into the use of alternative disinfectants such as ozone, permanganate and chlorine dioxide. Parallel to this effort, the same chemicals have received renewed attention as oxidants for the control of toxic organic compounds including THMs in water, and it is this work which is emphasized in the following sections.

Returning to the question of the oxidizing power of aqueous chlorine, it has been known for some time that prechlorination may enhance flocculation/sedimentation processes.[37] As early as 1924 Weston[38] discussed the beneficial aspects of prechlorination to improve floc formation. This property, combined with the power of chlorine to prevent biological growth in intake transmission lines, in settling basins, and on filter beds, has led to widespread use of the chemical in quantities far above those required for bacterial disinfection.

It is not known at this time what is the actual mechanism of oxidation of natural organics by aqueous chlorine. Recently, Christman, et al., in an EPA-sponsored study[39] have identified a series of oxidized, sometimes chlorinated compounds from the chlorination of aquatic humic acid. (Humic acid and fulvic acids are generic names for the largest fraction of organic material present in surface waters, soils and groundwater.[30]) Glaze and co-workers in another EPA-sponsored project have shown that chlorination increases the polarity of aquatic organic material so that it becomes less sorbable on non-polar synthetic resins.[40] In work from the group at Stanford University[41] also sponsored by EPA, organic halogen compounds produced during the advanced treatment of municipal wastewater were shown to be transported rapidly through the ground after well injection near Palo Alto, California. The results show these non-volatile compounds are quite polar and not adsorbed in the aquifer strata.

In principle, the oxidizing power of high concentrations of chlorine is sufficient to degrade many toxic substances. In fact, the use of large doses of chlorine (2000 mg/L to 4000 mg/L) for sludge destabilization is a commercial process.[42] Morris has suggested "that a partial solution to the problem of chlorinated organic compounds

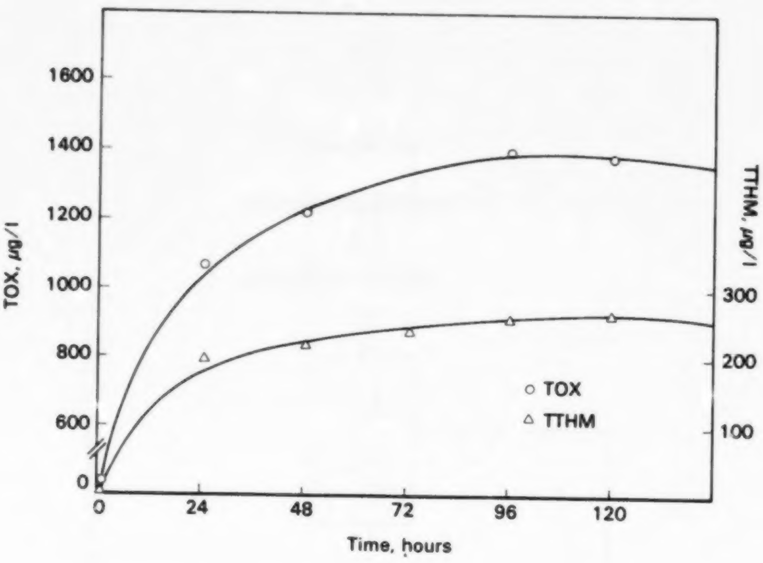


Figure 1. Formation of trihalomethanes and non-volatile organohalides by chlorination of filtered water from a surface source in southern United States (20 mg/L dose HOCl, pH 6.5, incubated at 26°C).

in. . . .drinking water is an intensification rather than an abatement of hypochlorination." However, it is unlikely that chlorine or hypochlorite will be used for this purpose in drinking water treatment. As shown above, chlorinated by-products such as THMs inevitably will be produced, and the risk to human health posed by these substances, however small, will probably deter further expansion of the use of chlorine as an oxidant. Recent attention has been focused on alternatives to chlorine for this purpose.

OZONATION[43-47, 49]

Ozone is not used extensively as a water treatment chemical in the United States, but because of its widespread use in Europe[48] the EPA has initiated numerous internal and extramural research projects to examine potential uses of ozonation. Many of these laboratory studies and pilot plant projects use ozone as a chemical oxidant. Four applications of ozonation for this purpose are possible:

1. Oxidation of natural organics as an aid to floc formation
2. Destruction of THM precursors prior to chlorination
3. Destruction of THMs and other toxic organic chemicals
4. Oxidation of natural and synthetic organic materials to enhance their biodegradability for removal on biological filters.

Ozone is generated on site,[50] usually by an electric discharge process in a flowing air or oxygen stream. Mixtures of 1% to 3% ozone/air and 3% to 5% ozone/oxygen are produced, which are then mixed with water in a manner to ensure efficient transfer into the liquid phase. Fig. 2 is a schematic diagram of a typical ozone generating and contacting system for water treatment.

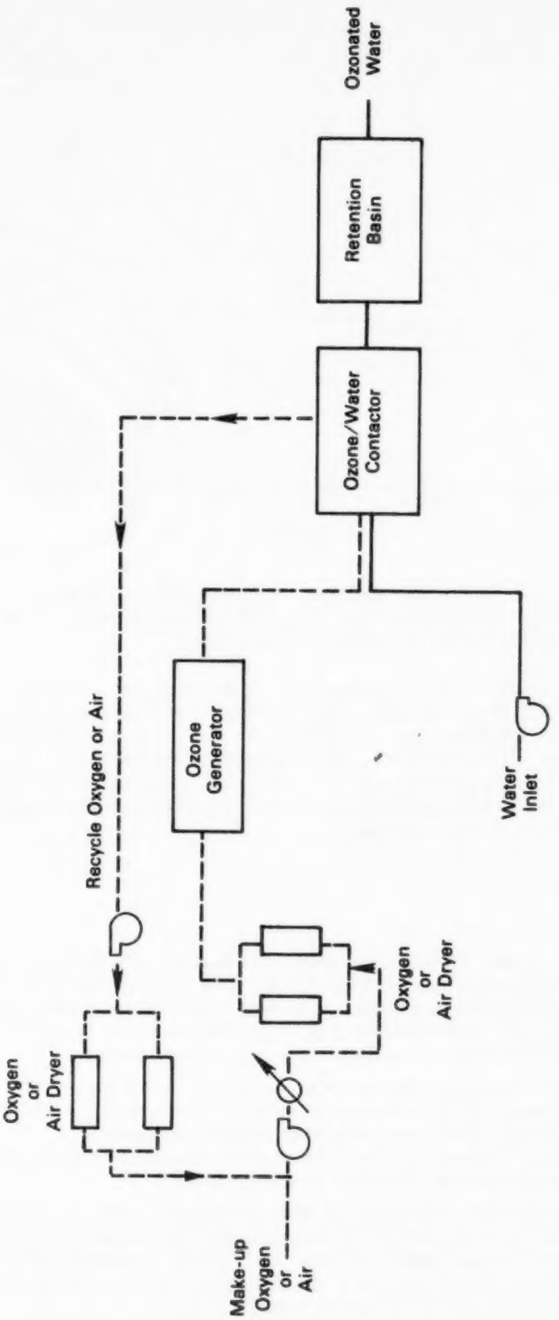
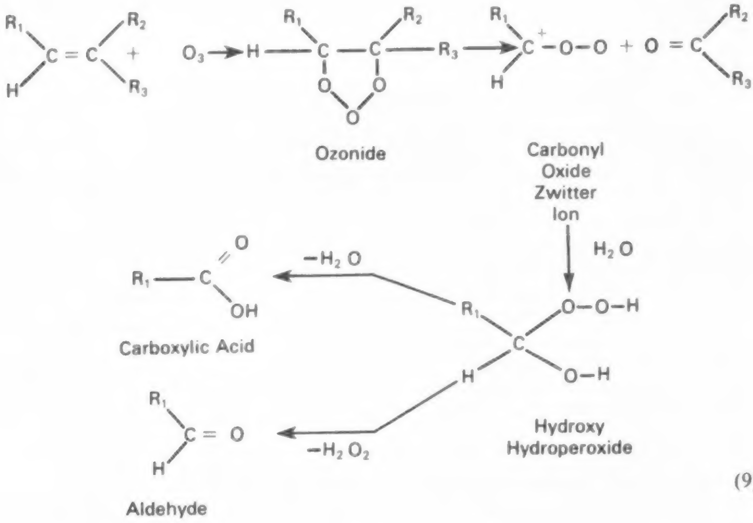

Ozonated Water
Retention Basin
Ozone/Water Contactor
Recycle Oxygen or Air
Ozone Generator
Water Inlet
Oxygen or Air Dryer
Oxygen or Air Dryer
Make-up Oxygen or Air

Figure 2. Schematic diagram of typical ozone generating and contacting facility for water treatment (After Rosen[50]).

As an oxidant, ozone is the most powerful of those used in water treatment, acting by at least two mechanisms in aqueous solution. At low pH values the ozone molecule O_3 directly attacks organic substances.[51,52] Being an electrophilic reagent, ozone is particularly active towards substances such as phenols which are activated to electrophilic attack. The ozone molecule also acts as a 1,3-dipole attacking unsaturated centers such as olefins to form unstable ozonides. These decompose in water to yield carbonyl compounds as shown in Equation (9).



(9)

The intermediate hydroxy hydroperoxide is usually decomposed rapidly in aqueous media, although in one case (from naphthalene) it is more long lived.[53]

At high pH values, ozone decomposes by a complex process yielding a variety of products such as oxygen and hydrogen peroxide. Hoigné and Bader have shown that ozone reactions at high pH involve the hydroxyl radical intermediate,[54,55] a very reactive, unselective oxidant. Some organic substrates, such as benzene, react much faster with the hydroxyl radical than with ozone. Others, such as phenol, are more reactive towards molecular ozone at low pH values. Most significant, the immediate oxidation by-products will be different in the two cases where different reaction pathways are taken.[56]

Ozone as an Aid to Color Removal and Flocculation

This property of ozone has not been exploited significantly in the United States, although it is well appreciated in Europe and Canada.[48,57] Only small doses of ozone are required to enhance floc formation, and in the process significant decrease of color is obtained. Sontheimer has attributed the effect to the oxidation of humic material in the water into a floc forming polyelectrolyte.[58] The beneficial effects of preozonation have been documented by Schwartz and co-workers,[59,60] by Trussell, et al.,[61] McBride,[62] Maier,[57] and Tate and Trussell.[63] Most significant are the advantages of preozonation in direct filtration systems, where improved flocculation is accompanied by lower THM values upon post-chlorination. It appears direct filtration plants with preozonation, followed by post-disinfection with chlorine, chlorine dioxide or chloroamines offer a viable alternative to conventional treatment for many applications.

Ozone for Destruction of THM Precursors Prior to Chlorination

THM precursor removal with ozone has not proven to be a satisfactory treatment method. This is due primarily to the fact that ozonation produces THM precursors as well as destroys them. This conclusion has been reached as the result of studies by Rook,[64] Riley, et al.,[65] Hubbs,[66] Glaze and co-workers,[67,68] and Love and others.[69] Fig. 3 shows the destruction of precursors in a continuous process at a pilot plant using water from a southern United States reservoir.[70] At these low dose rates THMFP destruction is minimal; however, at higher dose rates more extensive destruction of precursors may occur[68,69,71] as shown in Fig. 4.

Ozonolysis of Organic Micropollutants—

Ozone is selective in its ability to oxidize organic compounds in water, and in general the method has not proven to be useful for removal of these substances from water. There are, in fact, few published reports taken from actual plants or pilot plants with which to gauge ozone's effectiveness in this application.[72]

Sontheimer and co-workers[73] have reported data on the effect of ozonation of several organic halides in Rhine River water. Table 2 shows that only the trichlorobenzenes are removed by ozonation and filtration, whereas all of the halides are adsorbed by activated carbon. Ozonation has been shown to reduce the levels of low molecular organic halides such as trichloroethylene from reclaimed wastewater. However, the effect is largely due to purging in the ozonation process.[74] All of this does not discount the potential for removal of specific organic contaminants in certain cases where reactivity with ozone is high, as with certain carcinogens. In such cases, ozonation may prove to be a useful treatment alternative.[75]

Ozone Combined with Activated Carbon—

This subject is treated in more detail in the chapter by DiGiano. Suffice it to say here that many authorities feel that ozonation prior to activated carbon filtration improves the removal of organic constituents in the process.[58] While there is by no means full agreement on the mechanism of this process,[76] it is usually contended that ozonation partially oxidizes natural and anthropogenic compounds, making them more susceptible to biological metabolism on the filters.[77,78] Current research is being directed by the EPA and other agencies toward a more thorough understanding of the role of the preoxidant and of the mechanisms operating on carbon filters.

Cost of Ozonation in Water Treatment—

Ozonation is a rather expensive process by water treatment standards, requiring substantial capital investment and operating (energy) costs. Clark and co-workers at the EPA Municipal Environmental Research Laboratory (MERL) in Cincinnati have estimated the cost of ozonation facilities.[79] Design parameters are shown in Table 3 along with total costs for several size plants. The firm of Culp/Wesner/Culp independently calculated capital and O&M costs of ozonation plants in an EPA-sponsored project.[80] If one utilizes these data for a 10 MGD plant with a dose of 10 mg/L (a more realistic figure for organics control than 1 mg/L), the results are shown in Table 4. The cost estimates in Tables 3 and 4 are presumably out of date due to substantial increases in energy and other expenses which determine the net cost of producing ozone. Recent estimates by EPA suggest that the figures in Table 3 should be increased by approximately 20% and 100% for small (1 MGD) and large (100 MGD) plants respectively. While these costs are high by comparison with conventional unit processes, it should be noted that ozonation properly applied could save on chemical costs for disinfection and flocculation and possibly on reactivation costs for GAC filters.

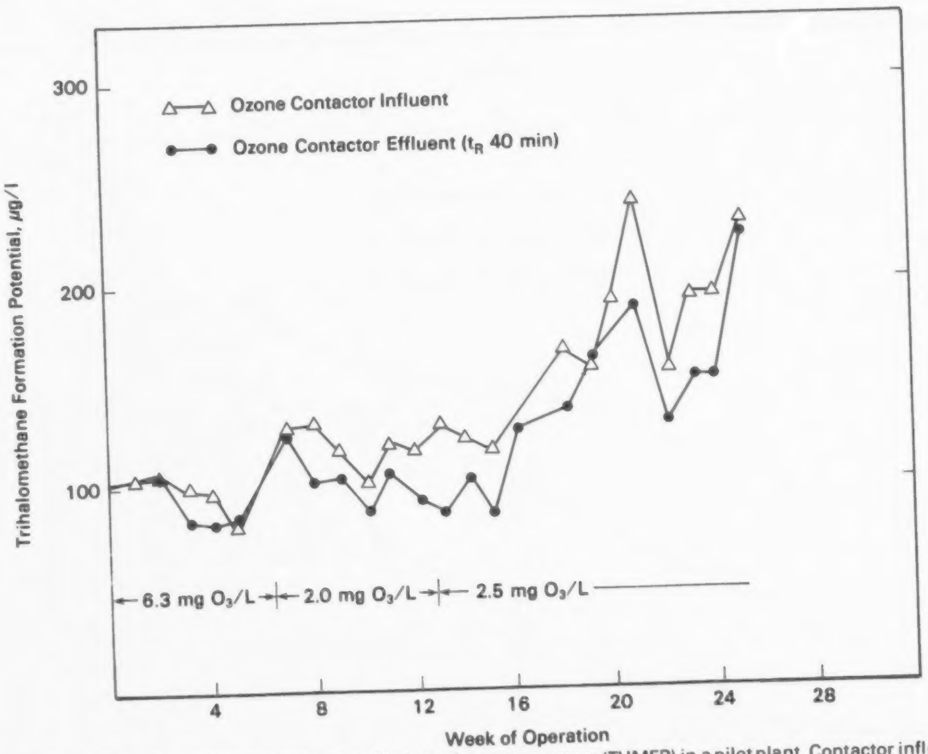


Figure 3. Effect of low doses of ozone on trihalomethane precursors (THMFP) in a pilot plant. Contactor influent is settled/filtered water at pH 5.5-6.5, TOC 2.7-4.6 mg/L. Contactor turbine type with 85-90% transfer efficiency. THMs measured after dose of 20 mg/L for 72 hours at pH 6.5.

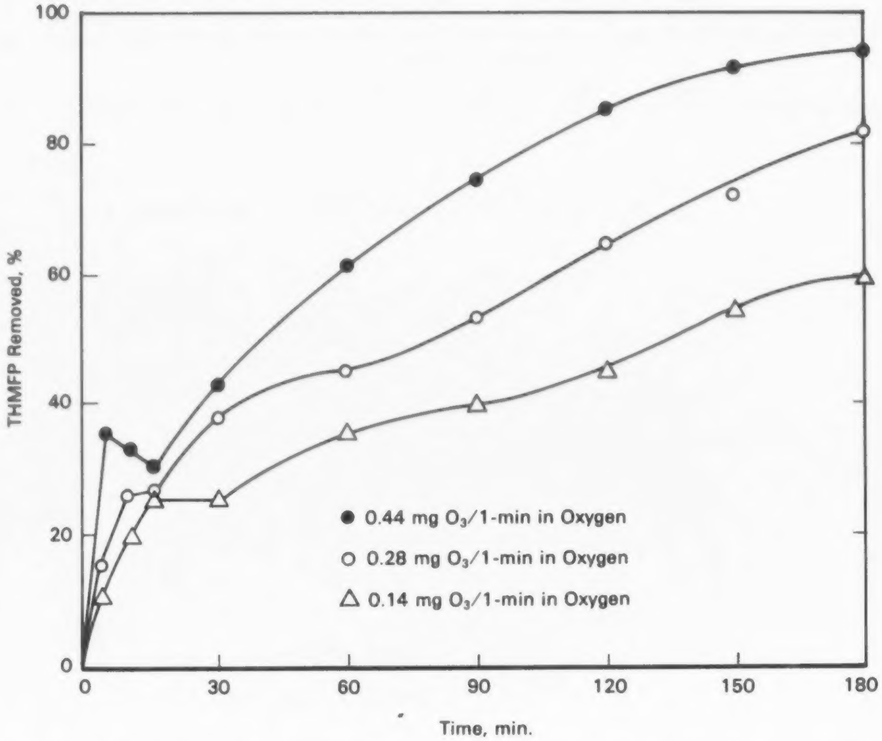


Figure 4. Effect of ozone dose on the destruction of trihalomethane precursors in water from the same source as Figure 3. THM's measured after dose of 20 mg/L for 72 hours at pH 6.5.

Table 2. Effect of Treatment Methods on Selected Organic Halides in River Rhine[73]

Substance	% Remaining in Effluent from		
	River Bank Filtration	Ozonation Plus Sand Filtration	GAC Filtration
Chlorobenzene	4	7	< 1
Dichlorobenzene (o,m,p)	38	42	5
Trichlorobenzene (3 isomers)	62	< 1	< 1
Chlorotoluene	6	9	< 1
Dichlorotoluene	38	38	< 1

Table 3. Design Parameters and Total Costs for Ozonation[79]

Ozone dose: 1 mg/L
Ozone contact time: 20 min.
Cost of oxygen: 0.046 $/lb
Construction cost index: 256.7
Wholesale price index: 178.1
Direct hourly wage rate: 5.19 $/hr
Amortization interest rate: 7 percent
Amortization period: 20 years
Electric power cost: $0.01/kwh
Capacity factor: 70 percent

Total cost (¢/1000 Gallon)		Plant size (MGD)
air	oxygen	
6.34	7.68	1
2.27	2.53	5
1.65	1.77	10
0.85	0.87	100
0.79	0.81	150

Summary of Advantages and Disadvantages of Ozone for Water Treatment—

The advantages and disadvantages of ozone for water treatment have been summarized by Sontheimer, from whom Table 5 is taken.[73] As a result of the European experience, United States research efforts on the applications of ozone have increased significantly in the past decade. At the present time these efforts emphasize ozonation in combination with activated carbon filters but further research using the full potential of ozone should be forthcoming.

Table 4. Estimated Costs for an Ozonation Facility for Removal of Toxic Organic Compounds

Design parameters

Ozone dose: 10 mg/L

Ozone contact time: 20 min.

Cost of oxygen: 0.050 $/lb.

Plant size: 10 MGD

Ozone utilization: 833 lb/day

Construction cost

Ozone generator:	$ 983,690*
Ozone contact chamber:	50,520†
TOTAL:	$ 1,034,210

Amortization periods: 20 years

Amortization interest rate: 7%

Amortized capital cost: $97,622/year

Operation and maintenance costs: $114,700‡/year

Oxygen cost: $18,250/year

Total cost: $230,572/year

Cost per 1000 gallons of water: 6.3¢

*Reference 80, Table 37; 1000 lb/day. †Reference 80, Table 38; 23000 ft^3.
‡Reference 80, Table 39; 1000 lb/day.

Table 5. Advantages and Disadvantages of Ozone in Drinking-Water Treatment[73]

Oxidation with Ozone	
Advantages	Disadvantages
Rapid disinfection and virus inactivation	High ozone consumption by organic substances
No commercial chemicals required	High investment and operating costs
Microflocculation; Formation of degradable organic substances	After-treatment step and installation required
Increase of polarity	Decrease of molecular weight
Transformation of resistant into biodegradable substances	Increased germ formation in distribution network
No formation of harmful substances	Biological after-treatment and safety chlorination required
Numerous processes and installations for ozone input	Difficult to control; Mass transfer often determines ozonation efficiency

CHLORINE DIOXIDE

Chlorine dioxide, like ozone, is a powerful disinfectant and oxidant. While not used as extensively as chlorine, it does find substantial application in portions of the world including locations in North America.[81] Chlorine dioxide is favored particularly in Belgium and other countries of Western Europe for disinfection of ground waters, for taste and odor control, and for control of iron and manganese.[81-83]

More recently, chlorine dioxide has been found to compare favorably with chlorine for predisinfection and oxidation of raw surface waters. Masschelein, a leading authority on the use of chlorine dioxide for water treatment, reports that costs for pretreatment at the Compagnie Intercommunale Bruxelloise favor chlorine dioxide over chlorine by a factor of 2.4.[82b]

Chlorine dioxide is receiving substantial attention by EPA authorities since it was established ClO_2 produces no trihalomethanes.[84] This property combined with its good disinfection potential has promoted chlorine dioxide to a position of prominence among the chemical oxidants.

Chlorine dioxide to be used in water treatment is prepared on site, usually from sodium chlorite.[82a,82b] Two methods are used; one described in Equation (10) involves disproportionation of chlorite in acidic media, usually hydrochloric acid:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \qquad (10)$$

Under appropriate reaction conditions, nearly quantitative yields of ClO_2 are achieved, although chlorite and sometimes chlorate are by-products. Fig. 5 shows a schematic diagram of a chlorine dioxide generator using this process.

Chlorine dioxide may also be produced by the oxidation of chlorite by chlorine (Equation 11).

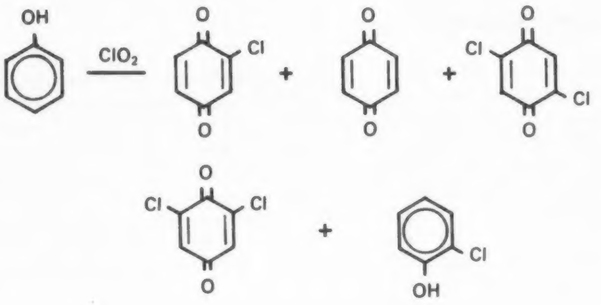
$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad (11)$$

Proper control of the mixing of the two reagents results in excellent yields of ClO_2, which may be fed directly into the water or stored for subsequent dosing (Fig. 6). Usually a slight excess of chlorine (10%) is recommended; however, this may have undesirable side effects (see below).

Formation of THMs and Other By-Products

Chlorine dioxide does not react with natural aquatic organic compounds to form trihalomethanes.[83-85] Fig. 7 taken from Stevens, et al.[85] from Miltner[84] shows no THM formation from ClO_2 with humic acid, a powerful THM precursor with hypochlorite. As expected, mixtures of chlorine dioxide and hypochlorite form THMs, but this is presumably due to the hypochlorite, not to chlorine dioxide.[83] Also shown for comparative purposes is the yield of THMs from chlorine alone.

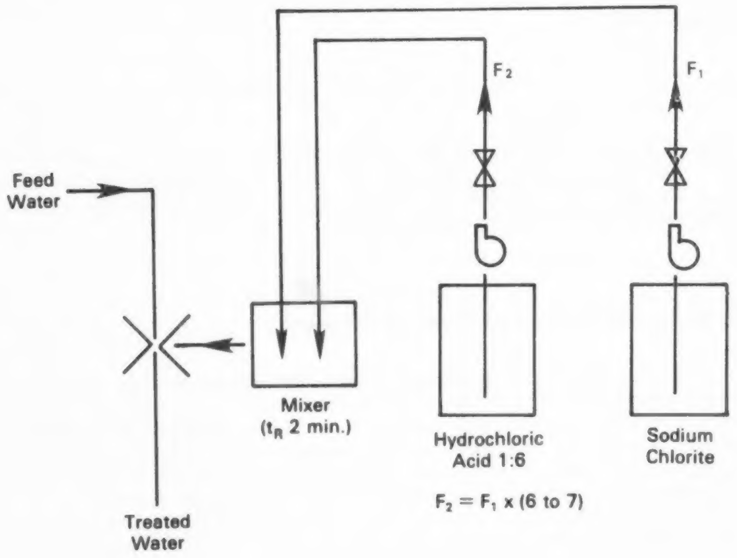
The absence of THM by-products does not mean that no chlorinated by-products are formed when ClO_2 reacts with raw waters. Stevens, et al.[85], Rosenblatt,[86] and Hedberg, et al.[83] have reviewed the chemistry of chlorine dioxide and all acknowledge that chlorinated derivatives are possible from a variety of chemical precursors. For example, chlorohydrins are reported from the reaction of chlorine dioxide with methyl oleate.[85] Phenol reportedly forms a series of quinones and chloro-quinones[87] (Equation 12).



(12)

More significant perhaps are the non-chlorinated epoxides reportedly formed from the reaction of chlorine dioxide with substituted olefins.[83] However, these substances have not been found in actual drinking waters treated with chlorine dioxide to this date.

Stevens and co-workers at the EPA MERL in Cincinnati have examined volatile by-products of Ohio River water treated with chlorine dioxide.[85] Low molecular weight aldehydes were the only by-products identified.



Feed Water
F2
F1
Mixer (tR 2 min.)
Hydrochloric Acid 1:6
Sodium Chlorite
F2 = F1 x (6 to 7)
Treated Water

Figure 5. Schematic diagram of typical facility for generation of chlorine dioxide from sodium chlorite and hydrochloric acid (From Masschelein[82b]).

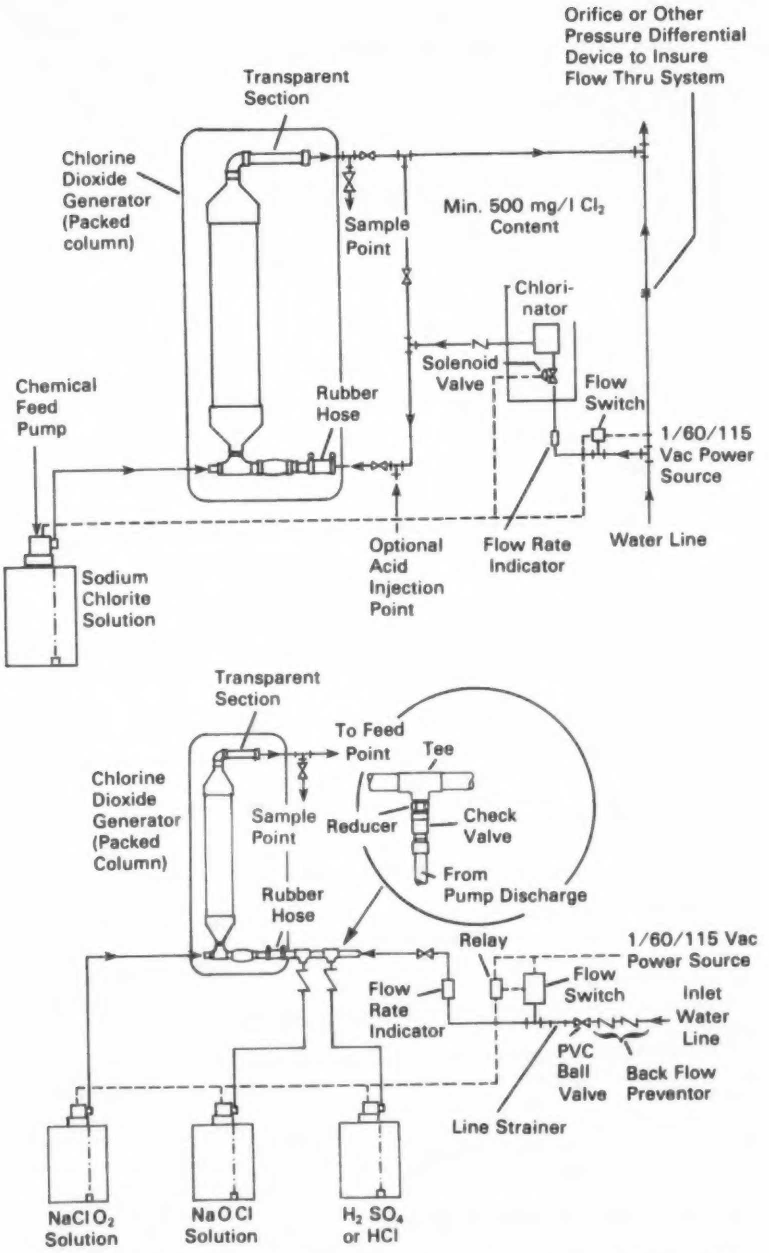

Orifice or Other Pressure Differential Device to Insure Flow Thru System
Transparent Section
Chlorine Dioxide Generator (Packed column)
Sample Point
Min. 500 mg/l Cl₂ Content
Chlori-nator
Solenoid Valve
Flow Switch
Chemical Feed Pump
Rubber Hose
1/60/115 Vac Power Source
Sodium Chlorite Solution
Optional Acid Injection Point
Flow Rate Indicator
Water Line
Transparent Section
To Feed Point
Tee
Chlorine Dioxide Generator (Packed Column)
Sample Point
Reducer
Check Valve
From Pump Discharge
Rubber Hose
Relay
1/60/115 Vac Power Source
Flow Switch
Flow Rate Indicator
Inlet Water Line
PVC Ball Valve
Back Flow Preventor
Line Strainer
NaClO₂ Solution
NaOCl Solution
H₂SO₄ or HCl

Figure 6. Schematic diagram of typical facility for generation of chlorine dioxide from chlorine and sodium chlorite (After Sussman and Rauh, In Ref. 47, p. 355).

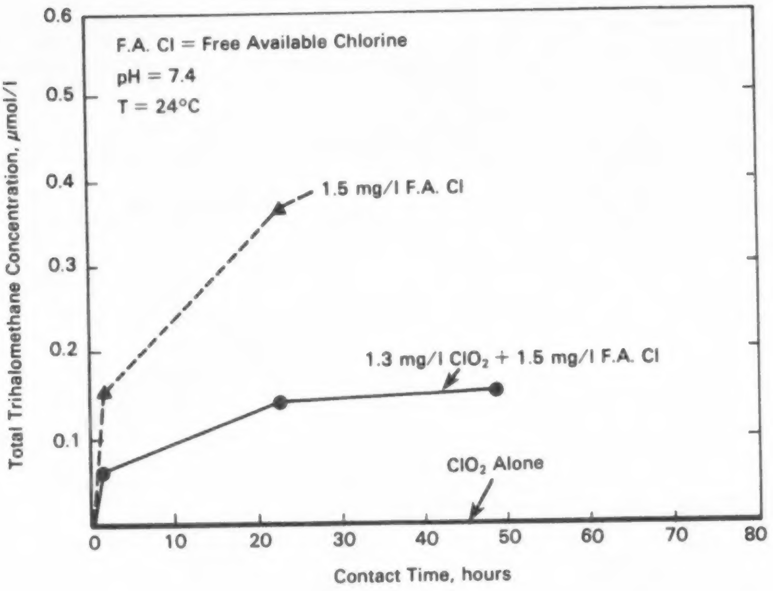


Figure 7. Trihalomethane formation by ClO_2 and excess free available chlorine, ERC pilot plant settled water (From Miltner[84]).

Chlorine Dioxide as an Oxidant in Water Treatment—

Chlorine dioxide is often used at low doses to control taste and odor compounds in water works.[88] In addition, ClO_2 reportedly oxidizes organic compounds such as 3,4-benzopyrene,[82a] yielding noncarcinogenic quinones.[89] The effect on pesticides is spotty, however; some compounds such as parathion are destroyed only with difficulty.[90] For the elimination of phenols from wastewaters, chlorine dioxide has been rated between ozone (best) and chlorine (poorest) in effectiveness.[91]

Hedberg and co-workers have reported interesting experiments on the effects of chlorine dioxide on haloform yields using raw water from the River Göta Alv in Sweden.[83] Fig. 8 shows that ClO_2 at reasonably low doses (<5 mg/L) substantially lowers the yield of $CHCl_3$ and $CHCl_2Br$ obtained by chlorination. The larger effect on chloroform yield may in some way by related to the oxidation of bromide, although it has been reported ClO_2 cannot oxidize bromide to bromine to a significant degree.[82a]

Perhaps the most important by-product formed when chlorine dioxide is used in water treatment is chlorite ion. Chlorite is known to cause methemoglobinemia, a condition in which hemoglobin is oxidized to a metabolically inactive (ferric) state.[93] After a careful assessment of the health effects literature, EPA officials have suggested limitations on the use of chlorine dioxide to keep the sum of residual oxidants (ClO_2, ClO_2^- and ClO_3^-) below 0.5 mg/L.[94]

Cost of Chlorine Dioxide Treatment

Clark, et al.[79] have calculated costs for 1 mg/L doses of chlorine dioxide in plants ranging from 1 to 150 MGD. Total costs range from 3.3¢/1000 gallons to 1.2¢/1000 gallons, respectively. Comparative costs for chlorine were calculated to be 3.1 to

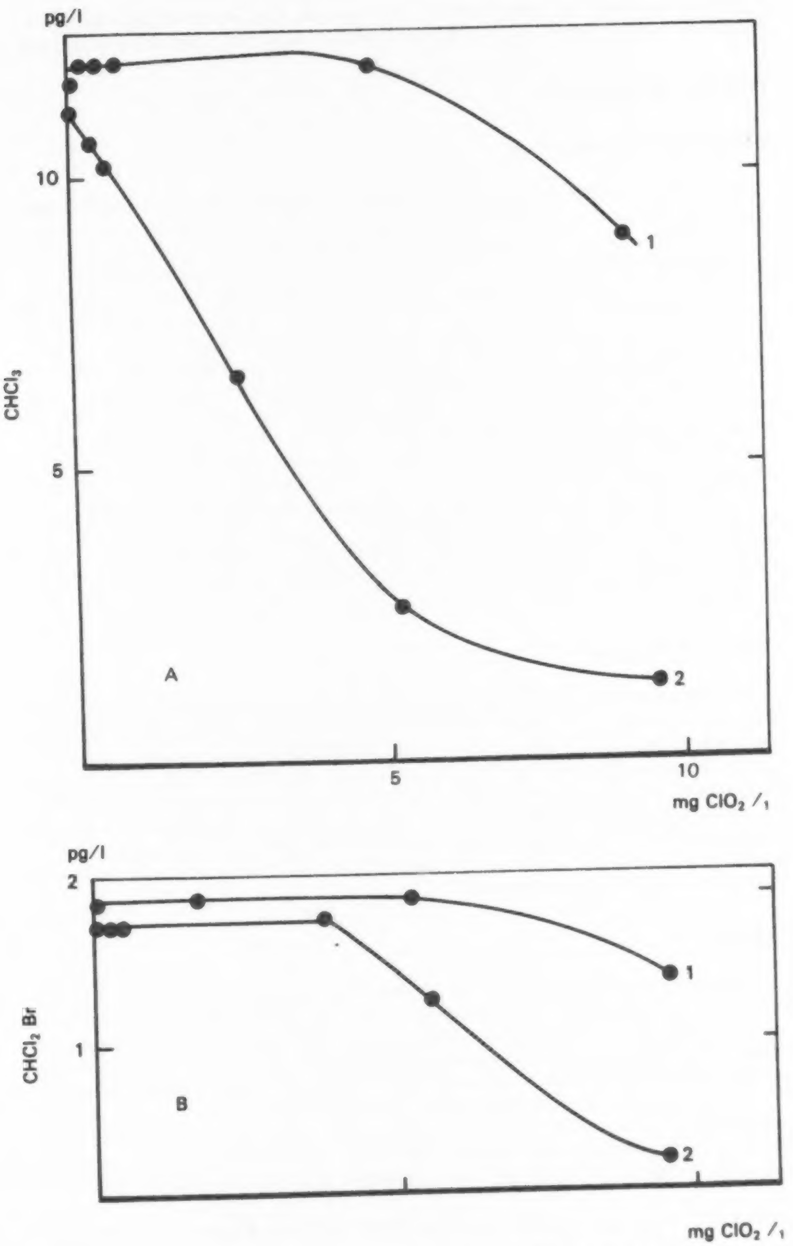


Figure 8. Formation of haloforms from combinations of chlorine and chlorine dioxide. A = $CHCl_3$; B=$CHCl_2Br$ 1 = chlorine added before chlorine dioxide; 2 = chlorine added after chlorine dioxide (From Hedberg, et al.[83]).

0.5¢/1000 gallons. As noted above, chlorine dioxide economy becomes more favorable for raw water treatment where its higher oxidative power can be exploited.

OTHER OXIDANTS

Potassium Permanganate

It has been reported that more than 250 North American and more than 30 European water works use potassium permanganate,[95] but it is not clear how many of these installations use permanganate sporadically and to what extent. Usually, permanganate application is limited to taste and odor control, and in some cases for lowering of iron, manganese, sulfide and phenol levels. Permanganate has also been used as a biocide to control algae growths in reservoirs.[95] Little work has been done on the control of organics with permanganate treatment. Singer and co-workers[96] studied trihalomethane formation potential (THMFP) reduction using raw water from Chapel Hill, N.C. and settled water from Durham. Both were non-chlorinated before treatment with $KMnO_4$. THMFP reductions were observed from 20 to 40 percent but doses of 10 mg/L permanganate were required to give the best results. The effect was greater at pH 10.3 than at 6.5. Voss and co-workers reported 83% reduction in chloroform formation levels using permanganate at an initial pH of 10.3.[97] However, the concentration of permanganate was 4.0×10^{-4} M (48 mg/L), an unrealistic dose level, and 3.5 hours contact time was allowed. Workers at the EPA MERL determined little effect on THMFP in Ohio River water using 5 mg/L doses of permanganate.[92] Fifteen percent removal of THMFP was observed with a 1.5 hour permanganate contact time.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a strong oxidant, but it has seen little use as a water treatment chemical. Overath has reviewed the applications of hydrogen peroxide in wastewater treatment, but cites no applications in drinking water technology except for disinfection.[98] Voss and co-workers[97] measured reduction of THMFP of Kansas River water, and were unable to detect chloroform (after 10 ppm chlorination) after treatment with peroxide. However, the dose was 1.1×10^{-3} M (37 mg/L), an unreasonably high level for water treatment purposes, and the contact time was 22 hours. Nonetheless, the results are promising and show that peroxide oxidation, as stated by Overath "invites application."[98]

Ferrate

While ferrate ion (FeO_4^{-2}) has received sporadic attention for many years, it has not proven to be a popular disinfectant or oxidant. In acidic media its oxidation potential is high, 2.2 V, marking the reagent as another one of promise. Waite and Gilbert have reviewed the preparation and properties of ferrate salts,[99] and pointed out that ferrate treated wastewaters clarify and decolorize "nearly instantaneously." Ferrate was found to significantly reduce the concentrations of allylbenzene, benzene chlorobenzene, and 1-hexene-4-ol. Voss, et al. found no dramatic decrease in THM precursors with ferrate treatment although simultaneous treatment of humic acid with ferrate and HOCl gave lower chloroform yields than HOCl alone.[97]

OZONE/UV AND OTHER CATALYTIC OXIDATION PROCESSES

While Overath may be correct in stating that hydrogen peroxide "invites application,"[98] it is the catalytic oxidation processes which are especially promising. These processes, which involve the generation of highly active chemical intermediates include the following:

- Ozone with ultraviolet radiation, the most studied and possibly the most promising catalytic oxidation process
- Hydrogen peroxide with ultraviolet radiation
- Hydrogen peroxide catalyzed ozonations
- Heavy metal catalyzed ozonation and peroxidations.

Ozone with Ultraviolet Radiation

This process has just been the subject of a three-year laboratory scale study by Glaze and co-workers.[100] The results confirm the power of the O_3/UV method for the destruction of THM precursors and other refractory organic compounds first suggested by Prengle and co-workers.[101a-d] The process is also being studied by a group at Westgate Research Corporation for application in reclamation of wastewaters[102] and has been applied to hospital wastewater constituents by Lee, et al.[103] and Chian and co-workers.[104a,b] As an example of the process, Fig. 9 shows the destruction of THM precursors with O_3/UV and O_3 only.[100] The effect of 0.31 Watts/liter UV radiation ($\lambda = 254$ nm) exceeds that of tripling the ozone dose rate. Prengle, et al.[101a-d] have estimated the cost for 90% removal of precursors from this system to be 10¢ to 14¢/1000 gallons. A pilot scale study to further examine the O_3/UV process for precursor removal is being conducted by SumX Corporation and the University of Texas at Dallas under EPA sponsorship (CR-808825-01).

Hydrogen Peroxide with Ultraviolet Radiation

Photolysis of hydrogen peroxide also generates active species, presumably hydroxyl radicals.[104] Berglind and co-workers[105] have described the oxidation of 3,4-benzopyrene, bromodichloromethane, methylisoborneol (a taste and odor compound) and chloroform. As shown in Table 6 the system is capable of removing these micropollutants rather effectively. Also shown in Table 6 is the effect of UV/H_2O_2 on color reduction in two humus samples. In other work, Ogata and co-workers[106] used the H_2O_2/UV process for destruction of non-ionic detergents. Later, Dore, et al.[107] compared ozonation and H_2O_2/UV for phenol oxidations and found the two processes to give comparable results. Cost data from Berglind, et al.[105] are not favorable, but the process deserves further investigation.

Hydrogen Peroxide Catalyzed Ozonation

Nakayama and co-workers have used hydrogen peroxide as a catalyst for increasing the effectiveness of ozonation.[108] Table 7 shows TOC reductions obtained for runs involving individual compounds initially at 40 mg/L and H_2O_2 at 30 mg/L. The results are favorable, although it should be noted that efficiencies should be much lower using solute concentrations in the ppb range which are more common in drinking water. The process was stated to be approximately one-half to one-third as expensive as GAC adsorption, but no details of the cost evaluations were given. Fernandes[109] is currently evaluating the O_3/H_2O_2 process for destruction of THM precursors.

Heavy Metal Catalzyed Ozonation and Peroxidation

Hydrogen peroxide decomposes in the presence of several types of catalysts and with UV irradiation into highly reactive intermediates. The most studied case is the Fe^{+2}/H_2O_2 system,referred to as the Fenton reagent.[110,111] Other heavy metals such

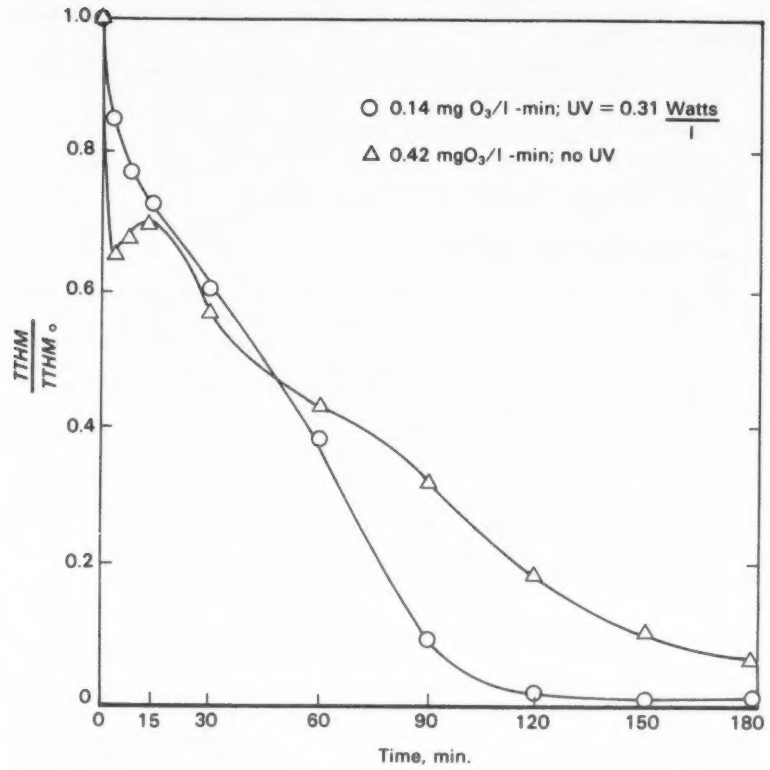


Figure 9. Normalized THM formation potential: ozone destruction of THM precursors-Caddo Lake water.[100]

Table 6. Removal of Organic Micropollutants With UV Radiation and Hydrogen Peroxide[103]

Period of UV Radiation (min.)	Percent of Compound							
	Without H_2O_2			With 0.0035% H_2O_2 (35 mg/L)				
	B(a)P	$CHCl_3$	$CHCl_2Br$	B(a)P	$CHCl_3$	$CHCl_2Br$	MIB	Color
0	0	0	0	0	0	0	0	0
30	–	–	–	–	25	42	100	
60	–	8	9	72	32	56		100*
120	29	58	25	91	91	91		100†
240	–	–	–	98	–	–		

*Sample "2", Fig. 5, Lee, et al.[103]
†Sample "1", Fig. 5, Lee, et al.[103]

Table 7. Pilot Scale Oxidation of Model Compounds with Ozone-Hydrogen Peroxide[108]

Compounds	TOC, mg/L Raw	TOC, mg/L Treated	$\Delta O_3/\Delta TOC$	$\Delta O_3/\Delta H_2O_2$
Methanol	37.5	2.3	12.9	15.2
Ethanol	38.4	8.3	11.0	11.0
n-Butanol	39.5	10.5	9.5	9.1
t-Butanol	39.0	10.5	9.8	9.1
s-Butanol	40.5	12.5	10.0	9.1
Sodium acetate	43.5	13.5	9.1	9.1
Propionic acid	43.0	7.5	6.9	8.3
Benzoic acid	44.2	11.1	11.1	12.3
Acetone	41.0	13.0	9.1	8.3
Methyl isobutyl ketone	45.3	20.7	9.9	8.3
Phenol	42.5	9.5	9.6	10.5
Ethanol amine	43.0	4.5	11.0	14.1
Diethanol amine	42.5	7.4	11.6	13.5
Ethylene glycol monomethyl ether	41.4	4.0	8.9	11.1

Initial concentration of substrates: 40 mg/L
Dose rate of H_2O_2: 30 mg/L
Solution flow rate: 23.9 mL/min.

as titanium (III)[112] catalyze H_2O_2 decomposition, and the active intermediate generally is assumed to be a hydroxyl radical (·OH). Hydroxyl radicals may also be generated by base catalyzed decomposition of ozone.[55] Ferric oxide has been used as a solid catalyst for increasing the efficiency of COD removal by ozonation.[113] While not thoroughly investigated, these and analogous systems are interesting and deserve further research.

FUTURE TRENDS

As noted in the introductory portion to this chapter, the future usefulness of oxidation processes will probably depend on the water quality criteria which are established. The promulgation of stricter standards for synthetic organics will most surely advance the need for advanced treatment processes such as oxidation. For this reason, and because of the need to evaluate alternatives to chlorine, oxidation processes should continue to be researched in the coming decade. Listed in Table 8 are some of the more obvious problem areas and exploratory topics which deserve attention. The list emphasizes identification of by-products and determination of their health effects; full scale evaluation of oxidation methods, particularly in nontraditional plant configurations; and basic research to develop novel catalytic oxidation methods. While certainly incomplete, the list is a formidable challenge to the scientific and engineering community and to the public who must eventually support this research effort.

Table 8. Research Issues Related to the Use of Oxidants in Drinking Water Treatment

By-product studies in pilot and full scale application of ozone, chlorine dioxide, and other oxidizing agents.

- emphasis on non-volatile and labile intermediates
- parallel studies of health effects of by-products and undifferentiated fractions

Pilot scale and full scale demonstration of ozone, chlorine dioxide and other available oxidants.

- emphasis on non-traditional configurations such as ozone with direct filtration; combinations of disinfectants with improved flocculation, etc.
- emphasis on standardization of water quality parameters, quality control procedures, and attention to process details such as ozone efficiency
- critical review of data to compare cost effectiveness on equal terms

Laboratory and pilot scale evaluation of novel oxidation systems.

- emphasis on basic research of catalytic oxidation processes
- comparison of by-products and health effects with uncatalyzed oxidation systems

ACKNOWLEDGEMENT

This work was carried out while the author was a member of the faculty at North Texas State University (NTSU), and represents the state-of-the-science of oxidation methods as of mid-1980. (However, it was possible during the process of editorial review to include selected papers appearing after this date.) Particular gratitude and pride is expressed for the work of staff of the NTSU Institute of Applied Sciences, including Sharon Dumas, Julie Kerestine and Sue Zant, and for the support of the Director, Dr. Kenneth Dickson. The author is also particularly indebted to editors of compendia and reviews which were used extensively in this work, especially references 7, 19, 43, 44, 46, and 47.

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REDUCTION OF ORGANIC SUBSTANCES IN MUNICIPAL WASTEWATER BY BIOLOGICAL PROCESSES

Robert L. Irvine, PhD

PERSPECTIVE AND APPROACH

A primary objective of a municipal wastewater treatment plant is the removal of organic compounds which have been discharged from residential communities, commercial establishments and industries. If these organics were allowed, instead, to flow untreated into a river or lake, the full impact and meaning of the term pollution would be witnessed. Under the most severe circumstances, oils, greases and other floatables would cover the surface along with mats of bottom sediment lifted to the surface by noxious gases produced by microorganisms thriving on the untreated organics. Such conditions were somewhat commonplace during the first half of the twentieth century and resulted in the reduction of activities, such as swimming and fishing, which are associated with natural bodies of water.

Because of efforts at both the local and federal level, steady progress towards limiting the nature and extent of discharge of organic pollutants was realized during the fifties and sixties. Intense interest in preserving the nation's waterways, however, did not blossom at the federal level until the late sixties. The notion that a body of water should be both fishable and swimmable was not established as a national goal until October 1972.

The agency responsible for implementing this national goal is the U.S. Environmental Protection Agency (EPA). EPA efforts during the seventies have included the establishment of national discharge limits, expansion and improvement of existing treatment facilities, construction of new plants, development of new treatment technologies and enforcement of regulations. An attempt is made herein to capture the essence of these efforts by combining the experience gained from existing treatment facilities with the insights being generated from on-going research.

Wastewater is comprised of a multitude of inorganic and organic compounds. This chapter will deal with the organic compounds. Technologies employed for the removal of organics are selected according to the physical, chemical and biological properties of the organics present in the wastewater. Simply stated, organics may be either soluble or insoluble. Some of the solubles have surface active properties which

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make them amenable to adsorption on materials such as activated carbon; others are volatile; many serve as a food source for microorganisms. Some exhibit all three properties. In addition to being either adsorbable or consumable, the insolubles can either settle, float or remain in suspension. This chapter will focus on those soluble and insoluble organics that are removed in the biological process.

The approach taken herein may be viewed as a severe departure from the classical descriptions available on the biological removal of organics from municipal wastewaters. This was done for several reasons. First, the EPA has produced, either directly or indirectly, an overwhelming collection of reports which cover adequately the classical approaches. While a summary of these techniques would properly satisfy the objectives of this chapter, the method employed provides a counter perspective for those engineers and scientists who are actively engaged in wastewater treatment. Second, the presentation is also directed at those who are not aware of the general principles and practices of wastewater treatment. The approach allows a rather high level technical discussion without demanding an understanding of specific techniques which are generally practiced in the field today. Third, another chapter in this monograph deals with the biological reduction of organics in industrial wastewaters. While the content of that chapter and this must overlap to some extent, overlap has been limited to the conceptual level with the content of one reinforcing that of the other. Finally, a decision was made to emphasize biological removal of organics from a process rather than a hardware point of view. This was easily accomplished with the method employed.

Eight new terms are introduced in this chapter. These are: INITIAL STATE, GOAL STATE, OPERATOR, MIX, SPLIT, SEPARATE, BIOLOGICAL REACT and CHEMICAL REACT. Each is fully capitalized both to avoid conflict with more common uses for the terms and to assist in clarity of presentation. In particular the entire organization of the chapter revolves around the use of four of the terms: INITIAL STATE, GOAL STATE, BIOLOGICAL REACT (sometimes designated as the OPERATOR: BIOLOGICAL REACT) and SEPARATE. In this context, the process notion of biological wastewater treatment is emphasized. At no time is criticism of more conventional presentation (generally used by the author himself) intended.

DEFINITION OF TERMS

A convenient way to visualize any process flowsheet was described by Powers[1] for chemical process synthesis and modified by Irvine[2] for use in water and wastewater treatment system descriptions. Simply stated, any treatment facility can be described in terms of an INITIAL STATE which is transformed into the GOAL STATE by the use of the proper sequence of OPERATORS (Fig. 1)*. The INITIAL STATE describes the concentration and amount of each chemical component in the raw materials stream that will be transformed in the process. The state (solid, liquid or gas) of each component is defined along with the temperature and pressure of the feed stream. The GOAL STATE is a characterization of the final products desired or achieved, once again in terms of concentration, amount, state, temperature and pressure. The unit operations and unit processes utilized to carry out the transformations desired are referred to as OPERATORS and are broadly classified as MIX, SPLIT, SEPARATE, and REACT (Fig. 2). MIX and SPLIT are simple terms for blending and separating streams. SEPARATE is primarily used to designate unit operations involved in phase separations such as in filtration,

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*The term OPERATOR is fully capitalized when used to designate a system function. Lower case is used to identify any individual (i.e., an operator) associated with the running of a treatment facility.

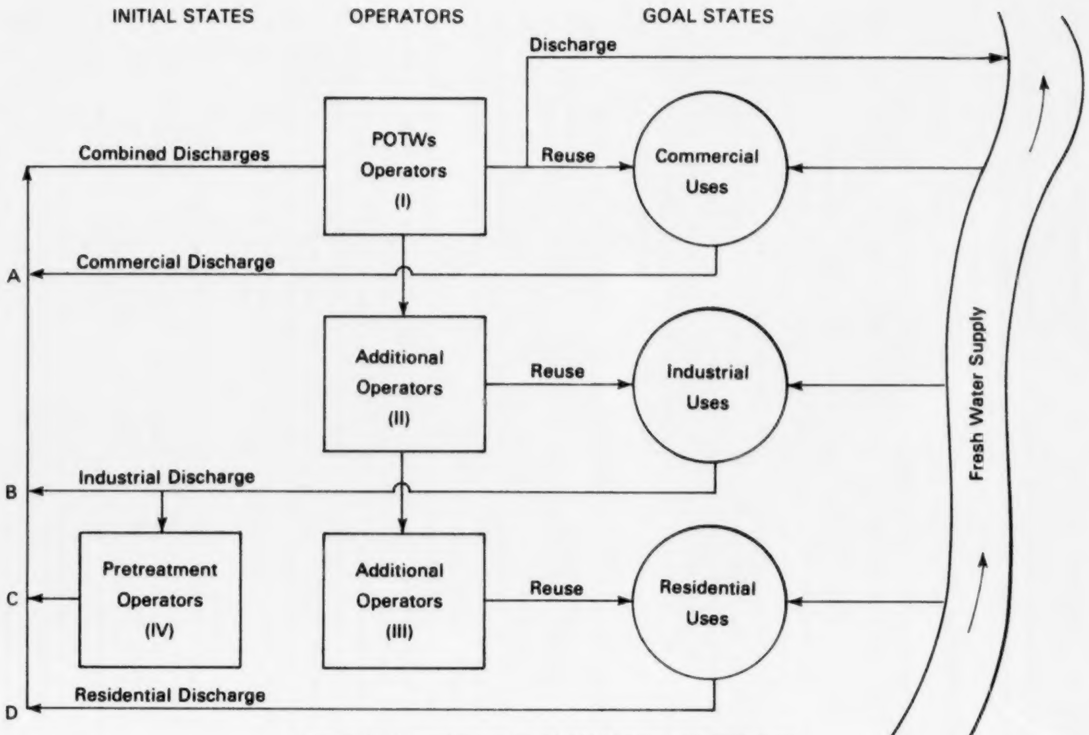
INITIAL STATES
OPERATORS
GOAL STATES
Discharge
Combined Discharges
POTWs Operators (I)
Reuse
Commercial Uses
A
Commercial Discharge
Additional Operators (II)
Reuse
Industrial Uses
Fresh Water Supply
B
Industrial Discharge
Pretreatment Operators (IV)
C
Additional Operators (III)
Reuse
Residential Uses
D
Residential Discharge

Figure 1. Transformation of initial state into goal state.

sedimentation and centrifugation. REACT may be either biologically or chemically mediated and defines the unit processes which transform one component into another.

Applied in this context, treatment of, say, groundwater for human consumption, industrial wastewater for reuse and municipal wastewater for surface water discharge, are conceptually the same, requiring the selection of the proper sequence of OPERATORS for the site specific INITIAL STATE and GOAL STATE. This generic similarity between all forms of treatment also provides the bases for describing the major differences among process flowsheets.

THE INITIAL STATE

The INITIAL STATE for municipal wastewaters is notably different from that for most industrial wastewaters. Indeed, depending upon the extent and nature of the industrial input and the degree of pretreatment practiced by each industry, the INITIAL STATE for one municipal wastewater can differ appreciably from that of another. In addition, urban runoff, inflow, infiltration and nature of the collection system all contribute to site specific variations in the INITIAL STATE. Nevertheless, municipal wastewaters are generally quite similar because contributions from households, restaurants, etc. vary little from site to site and normally constitute a notable fraction of the total wastewater flow (Table 1). As a result of these contributions, the concentration of total organics, measured as either Total Organic Carbon (TOC), Biological Oxygen Demand (BOD) or Chemical Oxygen Demand (COD), is relatively low, with the 5-day BOD ranging between 110 mg/L and 400 mg/L.[3]

Perhaps the most distinguishing feature of the INITIAL STATE of municipal wastewater is the presence of suspended solids (SS). Colloidal, supracolloidal and larger settleable particulate matter constitutes up to 75 percent[4] of the COD in municipal wastewater. Surprisingly, very little is known about the mechanisms involved in SS degradation, in spite of the fact that approximately 158 million out of the 220 million people in the United States are served by some form of central treatment facility[5] which must adequately handle these solids.

While the organic content of municipal wastewater has been generally characterized in terms of non-specific water quality parameters such as 5-day BOD and volatile suspended solids (VSS), recent efforts by the EPA to determine the treatability and removability of priority pollutants has resulted in the development of rather sophisticated analytical techniques for the measurement of organics.[6] The analytical procedures being developed are both complex and costly. Attempts to establish indicator or surrogate parameters such as BOD or TOC have not been successful.[7] As a result, organic priority pollutants have been used to define the

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Text for Figure 1: TRANSFORMATION OF INITIAL STATE INTO GOAL STATE is a phrase that may be applied to any treatment processes. Conceptually, a liquid stream containing water can be treated in such a manner that the water is extracted from that liquid. Because virtually all domestic wastewaters contain well over 99 percent water, unwanted inorganic and organic compounds are removed instead. The transformation then is one which converts an undesirable liquid stream having limited applications into one which has a multitude of uses. This notion is conceptually illustrated in Figure 1. In most cases, wastewater collected from residential, commercial and industrial sources are treated in a Publicly Owned Treatment Works (POTWs) and discharged to a receiving body of water. The extent of treatment required will determine the selection of OPERATORS needed for the conversion. If a more restrictive GOAL STATE limits must be met, other OPERATORS must be added. In the example shown above, commercial, industrial and residential discharges from points A thru D are collected for treatment in the POTWs(I). For purposes of illustration, the OPERATOR selection in (I) is shown to be adequate for both discharge and limited commercial use but additional treatment (II) is required for selected industrial use and still further treatment (III) for residential consumption. Industry may choose to treat its wastewater for direct discharge (not shown) to the receiving body of water or discharge without treatment (Point B) to the collection system or, if required, pretreat the wastewater to acceptable levels (IV) before discharging (Point C) to the collection system. The reader should note that the reuse described above is not generally practiced.

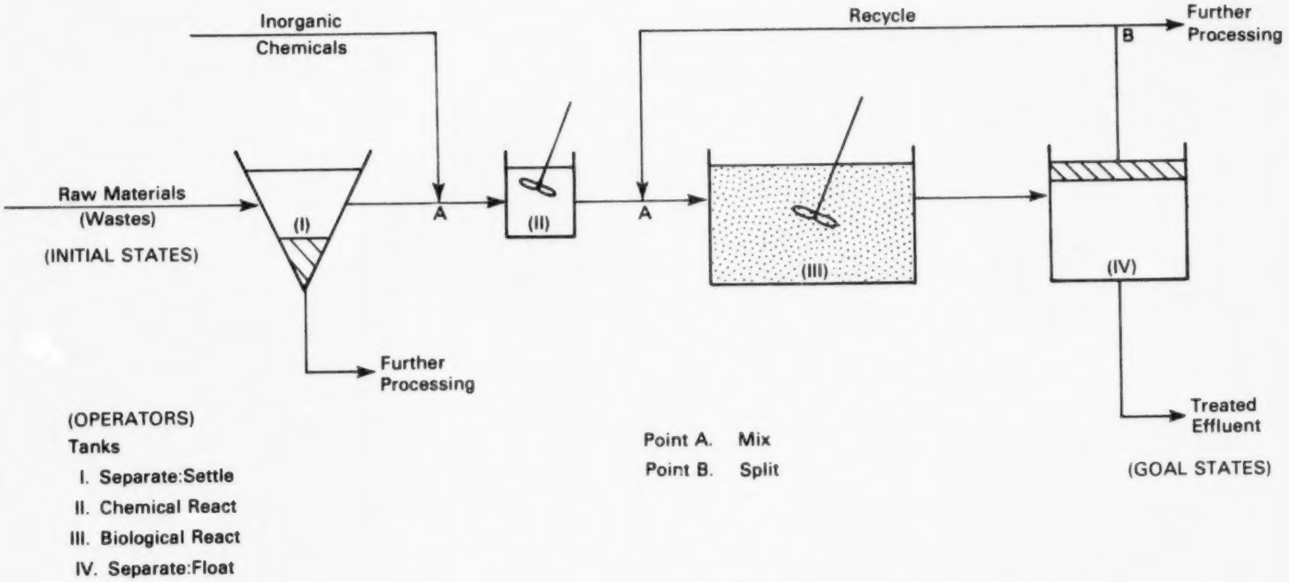
Inorganic
Chemicals
Recycle
Further
Processing
B
Raw Materials
(Wastes)
(INITIAL STATES)
(I)
A
(II)
A
(III)
(IV)
Further
Processing
Treated
Effluent
(OPERATORS)
Tanks
I. Separate:Settle
II. Chemical React
III. Biological React
IV. Separate:Float
Point A. Mix
Point B. Split
(GOAL STATES)

Figure 2. The sequence of operators.

Table 1. Typical Initial and Goal State

	Initial State		Goal State	
	Typical (mg/L)	Range (mg/L)	Typical (mg/L)	Range (mg/L)
Total 5-day BOD	200	50 to 400	20	5 to 30
Soluble BOD	80	0 to 200	None	None
TOC	150	50 to 300	None	None
COD	500	200 to 1000	None	None
SS	200	60 to 400	20	5 to 30
VSS	150	50 to 300	None	None

Text for Table 1: TYPICAL INITIAL AND GOAL STATE concentrations for municipal wastewater are given in Table I for various parameters used to report organics. The ranges shown reflect site specific variations which affect OPERATOR selection. Unless there is a significant industrial contribution, the INITIAL STATE will be defined by concentrations equal to or less than the typical values given. As a result, the sequence of OPERATORS in most POTWs is as follows: bar racks, screens, a grit chamber (this is a short detention time settler which removes high density particles such as sand and grit), a primary sedimentation tank, a biological reactor, a secondary sedimentation tank and chlorination. If properly designed and operated, this sequence of OPERATORS will meet or exceed the typical GOAL STATE shown. More stringent GOAL STATE criteria are usually imposed on effluents which enter a water quality limited segment of a body of water. A water quality limited segment is one in which typical effluent concentrations will impair the uses established for that segment. In such cases the OPERATOR sequence might be modified to include tanks for chemical reactions, additional sedimentation and filtration. It is interesting to note that there are usually no direct restrictions on soluble organic carbon. Only those organics which can be degraded in a typical biological reactor must be removed. The others are considered non-biodegradable and would require other methods (e.g., activated carbon) for removal.

INITIAL STATE of municipal wastewaters in limited cases. Nevertheless, the overall impact of expanding the INITIAL STATE to include priority pollutants should dramatically increase the understanding of removal mechanisms for other soluble and suspended organics and concomitantly improve the design and operability of treatment facilities.

THE GOAL STATE

Before the proper sequence in OPERATORS which will transform the INITIAL STATE into the GOAL STATE can be established, the GOAL STATE must be

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Text for Figure 2: THE SEQUENCE OF OPERATORS shown in Figure 2 has been selected to demonstrate the basic philosophy of treatment and is not necessarily typical of any POTWs. The first OPERATOR (I) allows for the sedimentation of a portion of the settleable solids. Such a tank is usually found in POTWs and is referred to as primary treatment. Bar racks and screens for the removal of larger debris often precede this tank. Some treatment facilities are required to remove phosphorus. Chemicals (typically either iron or aluminum salts) are mixed into the effluent from the primary sedimentation tank (I) at point A before entering tank (II). Reactions between the phosphorus and the salts added are allowed to occur in this tank. The reaction mixture containing suspended solids (SS) which were not separated in tank (I), precipitates of phosphorus formed in tank (II) and soluble matter are mixed with a recycle stream before entering tank (III). Microorganisms in this tank convert the organics into carbon dioxide, water and additional cell mass. Much of the insoluble matter is also incorporated into this mixed liquor. Finally, the discharge from tank (III) enters tank (IV) for separation of the solid matter (in this illustration by flotation but usually by sedimentation) from the treated effluent. The biological reactor (III) and the separator (IV) comprise what is called secondary treatment. In POTWs the treated effluent is chlorinated before discharge. Additional OPERATORS after the secondary system are called tertiary or advanced waste treatment. Solids separated in tanks (I) and (IV) require further processing. As can be seen from this illustration a basic philosophy of wastewater treatment is either the direct separation of SS or the chemical or biological conversion of soluble matter into SS for later separation.

defined. While the INITIAL STATE can be determined by sampling and analysis of existing wastewater flows and projecting population changes, the GOAL STATE is usually defined by some federal, state or local regulation. For example, a U.S. Court Consent Decree in 1976 between the Natural Resources Defense Council (NRDC) and the EPA[8] established the need for defining the GOAL STATE (and, therefore, the INITIAL STATE) in terms of priority pollutants (Table 2). The GOAL STATE must, of course, include limitations on organics in terms of the non-specific water quality parameters.

At the present time, the primary parameters defining the concentration of organics in the GOAL STATE are 5-day BOD and SS. Results presented in a U.S. Government General Accounting Office (GAO) study conducted in 1977,[9,10] however, indicated that 40% of all publicly owned treatment works (POTWs) failed to meet the designed GOAL STATE for 5-day BOD removals and 49% failed to meet SS removals. In all, only 50% of POTWs were in compliance with standards established by the National Pollution Discharge Elimination System (NPDES).

In a study conducted by the EPA's Office of Research and Development between June, 1975 and December, 1977[10,11,12], 287 waste treatment facilities were surveyed to determine the specific causes of failure to meet the desired GOAL STATE. Results from the 103 facilities selected for extensive study indicated that the major causes of poor plant performance were (1) inadequate plant operation and (2) plant design deficiencies. The poor plant performance resulted directly from factors which include the following: inadequate operator application of concepts and process control testing; lack of operator understanding of wastewater treatment; improper technical guidance; and, design limitations in the areas of infiltration/inflow, sludge wasting and return, aeration capacity and general process controllability and flexibility. Only 37 of the 103 plants evaluated met the NPDES GOAL STATE consistently. The report noted that an estimated 51 additional plants would be able, however, to meet NPDES GOAL STATE standards by implementing changes in operation and/or minor modification of design features. As a result of this study, the EPA recommended a Composite Correction Program (CCP) for improving the performance of existing facilities. This program was implemented at several sites with considerable success noted (Table 3). The CCP developed in this study has been adopted by the USEPA's Office of Enforcement as a part of a national enforcement strategy for POTWs GOAL STATE compliance.

An obvious conclusion for the CCP is that the OPERATORS (i.e., unit operations and processes) used at POTWs for biological reduction of organics are fundamentally sound and, if placed in the proper sequence, can transform the INITIAL STATE into the desired GOAL STATE at least in terms of 5-day BOD and SS. As is described below, more information is required before the impact of POTWs on the removal of organic priority pollutants can be assessed.

Organic Priority Pollutants

A preliminary study to obtain data on the occurrence of eight organic priority pollutants in the influent and effluent of two treatment plants was conducted in 1976.[13] Results from this rather limited study indicated that the concentrations of the organic priority pollutants tested were highly variable and that the EPA must improve the then existing analytical methods for organic priority pollutant measurement. Recently, four major studies were initiated by the EPA[14] to expand the data base for the occurrence and removal of organic priority pollutants in municipal wastewater treatment plants (Table 4). Two of these studies were conducted by the EPA Municipal Environmental Research Laboratory (MERL) in Cincinnati. One was a 25 city survey designed to refine analytical procedures and assess removability by analyzing data from one 24-hour composite collected from each influent and effluent. Results from this study indicate that unless the treatment plant discharge is diluted by a factor of 50 in the mixing zone, the concentration of several

Table 2. Selected Actions Influencing Goal State Limits

Name	Date	Selected Key Points
Consent Decree	1976	Established priority pollutant list
Resource Conservation and Recovery Act (PL 94-580)	1976	Identifies hazardous municipal sludges and solid wastes Regulates treatment, storage and disposal of hazardous wastes
Toxic Substances Control Act (PL 94-469)	1976	Regulates manufacture, processing, distribution, use and disposal of hazardous chemical substances
Clean Water Act (PL 95-217)	1977	Amended act passed in 1972 (PL 92-500) Identifies construction grants program, general effluent limitations, pretreatment requirements, toxic pollutant list, innovative and alternative technologies, and NPDES permits

Text for Table 2: SELECTED ACTIONS INFLUENCING GOAL STATE LIMITS for the control of organics are listed in Table 2. In the three laws, Congress identified the terms hazardous wastes, hazardous chemicals and toxic pollutants. The U.S. court consent decree defined the term priority pollutant. Thousands upon thousands of organic chemicals are included on lists which combine these terms. There is also considerable overlap among lists. Through the Toxic Substances Control Act, the EPA can prohibit or limit the manufacture of chemicals which pose an unreasonable risk to the public welfare. Highly concentrated hazardous wastes (e.g., waste liquid organics placed in drums for storage) are controlled by the EPA through the Resource Conservation and Recovery Act. Both acts help to exclude such compounds from municipal wastewaters. The organic priority pollutants are just 114 of the many organics which could have been identified for control under the Clean Water Act. In this sense the list is somewhat arbitrary. For example, solvents, cleaning agents used in the home, household paints, etc. contain a multitude of organic chemicals which may or may not be included on the priority pollutants list. Using the National Pollution Discharge Elimination System (NPDES) permit program described by the Clean Water Act, the EPA can enforce national standards for the removal of the selected organics on the priority pollutant list. Present GOAL STATE limits normally include "conventional" pollutants only. On-going studies will be used to determine the need for including specific organic compounds in these limits.

of the organic priority pollutants are likely to exceed proposed water quality criteria. The other MERL study involved pilot plant investigations at the EPA's Test and Evaluation Facility in Cincinnati to assess the effectiveness of conventional municipal waste treatment processes in removing priority pollutants. Selected organic priority pollutants were spiked into the raw wastewater. Typical removals ranged from 95% to 99%. This does not guarantee, however, that the discharge would not be either acutely or chronically toxic to aquatic organisms. Futhermore, the concentration of many compounds could exceed the proposed water quality criteria. Additional research is presently being conducted at this test and evaluation facility.

The remaining two EPA studies are being conducted by the Washington Headquarters Office of Water Planning and Standards.[14,15] One is a 40 city survey similar to the Municipal Environmental Research Laboratory, Cincinnati, OH (MERL's) 25 city survey. The notable difference is that each plant will be sampled for one week rather than one day. Preliminary results indicate that five organic priority pollutants (benzene, chloroform, bis (2-ethylhexyl) phthalate, tetrachloroethylene and toluene) are in all wastewaters, including those of domestic origin, and five additional organics (1,1-dichloroethylene, ethyl-benzene, butyl benzyl phthalate, di-n-butyl phthalate and trichlorylethylene) were consistently detected. More priority

Table 3. The Improved Performance Resulting from CCP

	Effluent Total 5-day BOD (kg/d)		Effluent Total SS (kg/d)	
Facility	Before	After	Before	After
A	160	51	154	41
B	136	15	273	9
C	35	10	70	4
D	75	33	111	49

Text for Table 3: THE IMPROVED PERFORMANCE RESULTING FROM CCP is dramatically illustrated in Table 3 for four different POTWs. Consider, for example, the improvement in the discharge of SS from facility **B**. On a yearly basis, facility **B** discharged 96,000 kg (over 100 tons) less solids into the receiving body of water after the implementation of CCP. Similar successes are noted for the other facilities for both 5-day BOD and SS. These results confirm the importance of a basic understanding of the biological process in design and operation. Many existing treatment facilities are quite capable of meeting present-day GOAL STATE limits without costly plant expansion programs. Of course some systems are extended in terms of aeration capacity, solids loading to the secondary sedimentation tanks and sludge handling and require some form of plant expansion.

Table 4. The List of Organic Priority Pollutants

Compounds	Limit of Detection* μg/L
Purgeable Organics by Purge and Trap	
Acrolein†	100
Acrylonitrile†	100
Benzene	10
Bromodichloromethane	10
Bromoform	10
Bromomethane	10
Carbon Tetrachloride	10
Chlorobenzene	10
Chloroethane	10
2-Chloroethylvinyl ether	10
Chloroform	10
Chloromethane	10
Dibromochloromethane	10
1,1-Dichloroethane	10
1,2-Dichloroethane	10
1,1-Dichloroethene	10
trans 1,2-Dichloroethene	10
1,2-Dichloropropane	10
cis 1,3-Dichloropropene	10
trans 1,3-Dichlorpropene	10
Ethylbenzene	10
Methylene chloride	10
1,1,2,2-Tetrachloroethane	10
Tetrachloroethene	10

1,1,1-Trichloroethane	10
1,1,2-Trichloroethane	10
Trichloroethene	10
Trichlorofluoromethane	10
Toluene	10
Vinyl chloride	10

Extractable Organics

Acid Extractables

4-Chloro-3-methylphenol	25
2-Chlorophenol	25
2,4-Dichlorophenol	25
2,4-Dimethylphenol	25
2,4-Dinitrophenol	250
2-Methyl-4,6-dinitrophenol	250
2-Nitrophenol	25
4-Nitrophenol	25
Pentachlorophenol	25
Phenol	25
2,4,6-Trichlorophenol	25

Base-Neutral Extractables

Acenaphthene	10
Acenaphthylene	10
Anthracene	10
Benzo(a)anthracene	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Benzo(g,h,i)perylene	25
Benzidine	10
Bis(2-chloroethyl)ether	10
Bis(2-chloroethoxy)methane	10
Bis(2-ethylhexyl)phthalate	10
Bis(2-chloroisopropyl)ether	10
4-Bromophenyl phenyl ether	10
Butyl benzl phthalate	10
2-Chloronapthalene	10
4-Chlorophenyl phenyl ether	10
Chrysene	10
Dibenzo(a,h)anthracene	25
Di-n-butylphthalate	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
3,3-Dichlorobenzidine	10
Diethylphthalate	10
Dimethylphthalate	10
2,4-Dinitrotoluene	10
Dioctylphthalate	10
1,2-Diphenylhydrazine	10
Fluoranthane	-
Flourene	10
Hexachlorobenzene	10
Hexachlorobutadiene	10
Hexachloroethane	10
Hexachlorocyclopentadiene	10
Indeno(1,2,3-cd)pyrene	25
Isophorone	10
Naphthalene	10
Nitrobenzene	10
N-Nitrosodimethylamine	-

N-Nitrosodi-n-propylamine	10
N-Nitrosodiphenylamine	10
Phenanthrene	10
Pyrene	10
2,3,7,8-Tetrachlorodibenzo-p-dioxin	0.003‡
1,2,4-Trichlorobenzene	10
Pesticides and PCB Extractables	
Aldrin	10
a-BHC	10
b-BHC	10
d-BHC	10
g-BHC	10
Chlordane (multi-component)	–
4,4′-DDD	10
4,4′-DDE	10
4,4′-DDT	10
Dieldrin	10
Endosulfan I	10
Endosulfan II	10
Endosulfan Sulfate	10
Endrin	10
Endrin Aldehyde	10
Heptachlor	10
Heptachlor Epoxide	10
Toxaphene (multi-component)	–
PCB-1016 (multi-component)	–
PCB-1221 (multi-component)	–
PCB-1232 (multi-component)	–
PCB-1242 (multi-component)	–
PCB-1248 (multi-component)	–
PCB-1254 (multi-component)	–
PCB-1260 (multi-component)	–

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*This is a minimum level at which the entire system must give recognizable mass spectra and acceptable calibration points.

†Detection limits refers to either the GC/MS method or direct aqueous injection (GC-FID).

‡Detection limit for both electron capture and GC/MS detectors.

Text for Table 4: THE LIST OF ORGANIC PRIORITY POLLUTANTS shown in Table 4 is divided into categories which correspond to analytical procedures used to identify them[6]. A thorough explanation of the analytical techniques for the measurement of organic priority pollutants may be found in that reference. A conceptual overview of these procedures is presented here. A municipal wastewater contains many organic compounds. The organic priority pollutants must be separated from the other compounds first, then from each other before being identified and quantified. Separate clean-up procedures for removal of background organics are usually not necessary for municipal wastewaters. The volatile (purgeable) organics can be purged from a wastewater sample with either helium or nitrogen gas, trapped and then separated in a gas chromatograph (GC). The extractable organics are extracted from a wastewater sample with methylene chloride at pH 11 for the base and neutral extractables and at pH 2 for the acid extractables, dried and concentrated before being separated in the GC. A modified procedure for the pesticide and PCB base/neutral extractables has also been employed. A mass spectrometer (MS) is used to identify and quantify the organics after separation. Some organics require special clean-up procedures while others need different extraction and separation techniques (e.g., high pressure liquid chromatography). In general, these procedures are quite time consuming and costly and must be performed in laboratories containing highly specialized equipment.

pollutants were found in the influent to larger municipal facilities than smaller ones having a lower industrial contribution. The final major study is a six city survey designed to determine the sources of priority pollutants (i.e., domestic, commercial or industrial). To date, four locations have been sampled. These are Muddy Creek Drainage Basin, Cincinnati, Ohio; Coldwater Creek Drainage Basin, St. Louis, Missouri; R.M. Clayton Drainage Basin, Atlanta, Georgia; and the Hartford Water Pollution Control Plant, Hartford, Connecticut. A collective summary of findings from these surveys is not yet available.

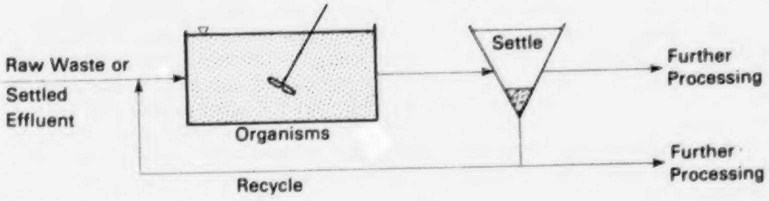
THE BIOLOGICAL PROCESS

OPERATOR selection for municipal wastewater treatment plants depends upon more than the parameters dealing with organics. Very often the INITIAL STATE and the GOAL STATE are defined in terms of additional components such as the various forms of nitrogen and phosphorus. As a result, OPERATOR selection, sizing and operation may reflect requirements based on the removal of components other than organics. Nevertheless, virtually all POTWs not involving land treatment consists of two OPERATORS: BIOLOGICAL REACT and SEPARATE. In particular, the biological removal of organics is intimately associated with some form of phase separation system, typically either sedimentation or flotation. Filtration is usually not employed unless some rather restrictive GOAL STATE for SS is mandated. Land treatment, on the other hand, is primarily associated with the OPERATOR: BIOLOGICAL REACT, in which soil organisms utilize the organics applied.

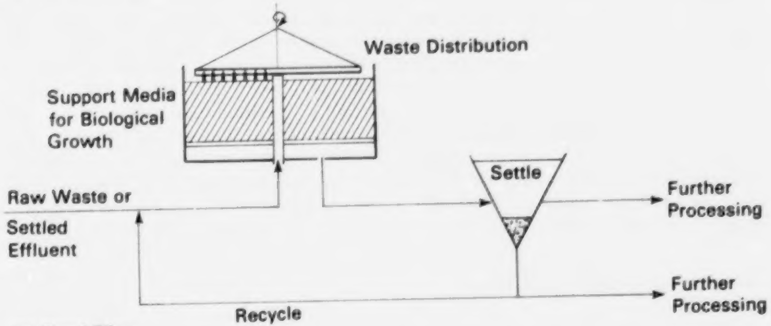
The primary function of any municipal wastewater treatment facility is the removal of soluble and insoluble organics from the raw waste flow. Because of the many different organic compounds involved (indeed, there are 114 priority pollutants alone), any combination of unit operations and chemical additions is either too costly or too difficult to permit ready and consistent removal of the organics present. As a result, BIOLOGICAL REACT, the conversion of soluble organics to microorganisms, carbon dioxide, water and other end products, is employed (Fig. 3). A principal objective of the treatment system is, therefore, the conversion of soluble organics into microorganisms which in turn constitute an insoluble mass that can be separated physically from the wastewater flow by some OPERATOR:SEPARATE. Some of the organics, however, are volatile and may be stripped from the system and, thus, avoid biological degradation. The volatile priority pollutants fit, of course, into this category. Insoluble organic compounds usually become enmeshed or adsorbed in the biological mass and are degraded to a lesser or greater extent depending upon the treatment system involved.

The microorganisms are typically grown either in suspension or attached to some surface. The systems may operate either in the presence of oxygen (aerobic) or some other electron acceptor (anoxic) or in the absence of an external electron acceptor (anaerobic). The rate of conversion of raw materials to end products depends upon a multitude of factors including the concentration of the various components involved in the reaction (e.g., substrate, microorganisms, inorganic nitrogen and phosphorus and oxygen), temperature, pH and the nature and distribution of the organics involved. The nature of the end products varies considerably with the environmental conditions imposed. For example, under anaerobic conditions low molecular weight acids, alcohols, aldehydes and methane gas are often produced along with a relatively small quantity of organisms, carbon dioxide and water while larger quantities of organisms, carbon dioxide and water are produced aerobically.

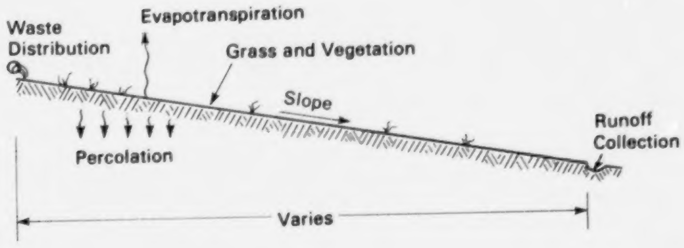
A complete story cannot be told by visualizing the OPERATOR:BIOLOGICAL REACT in a municipal wastewater treatment facility as either suspended or attached or as aerobic, anoxic or anaerobic. In aerobic suspended growth systems, for example, the microorganisms come together in large flocs. The depth of penetration of oxygen and organics depends, among other factors, upon the


Raw Waste or
Settled
Effluent
Organisms
Settle
Further
Processing
Further
Processing
Recycle

(a) Suspended Growth


Waste Distribution
Support Media
for Biological
Growth
Settle
Raw Waste or
Settled
Effluent
Further
Processing
Further
Processing
Recycle

(b) Fixed Film


Waste
Distribution
Evapotranspiration
Grass and Vegetation
Slope
Percolation
Runoff
Collection
Varies

(c) Overland Flow

Figure 3. The biological utilization of organics.

Text for Figure 3: THE BIOLOGICAL UTILIZATION OF ORGANICS can be conducted in a wide variety of controlled environments. Figure 3 shows three such systems. In all cases, the reactions which would otherwise take place at a slow rate in the dilute environment of a receiving body of water are accelerated in a controlled system by providing increased concentrations of both organics and microorganisms. As a result, organics can be utilized in a relatively small area as compared to that necessary in a river or lake without interfering with other uses such as recreation or fishing. In both the suspended growth and fixed film systems the secondary sedimentation tank is an essential feature. Unless the organisms produced and the SS captured are removed from the wastewater flow, GOAL STATE limits will not be met. In many treatment plants, especially suspended growth facilities, overall treatment plant performance is controlled by the operability of the sedimentation tank. Proper operation of the biological reactor is necessary for the enhancement of organisms with reasonably good settling characteristics. In the case of the suspended growth system, organisms and wastewater are usually aerated in the reactor with either mechanical mixers or compressed air. Wastewater is distributed over organisms attached to a support medium in the fixed film system. Treated water is recycled to the reactor in order to maintain a relatively constant hydraulic load on the bio-film and to provide the mixing and oxygen transfer which results from the free fall of fluid over the bio-film. The overland flow system is one of several land application facilities available. In this case, there is limited percolation of water thru the soil with the bulk of the reactions taking place near the soil surface as the wastewater flows down the incline (e.g., a hill with a two to four percent slope).

concentration of each in the bulk fluid. Depending upon the rate of substrate supply per unit mass of organisms present (this is often referred to as the mass loading) and the rate of aeration, the relative depth of substrate versus oxygen penetration in the floc may switch from hour to hour and from location to location within the entire reactor system. These temporal and spatial variations occur in attached growth systems as well. The extent to which these variations are allowed and controlled determines which reactions are occurring and which are responsible for overall plant behavior. As a result, two treatment plants receiving essentially the same waste and employing the same sequence of OPERATORS, may have notably different performance records.

BIOLOGICAL REACT for organic removal in most municipal wastewater treatment plants is aerobic with either suspended growth or fixed film (attached) system employed. Even though the innovative and alternative program implemented by the EPA promotes land treatment,[16] only a small fraction of the total number of facilities involves such systems. In particular, of the 158 million people serviced by 20,666 central collection systems carrying a total of approximately 22 billion gallons each day, 2,603 systems are without any form of treatment at all, 2,377 employ physical OPERATORS only, 3,331 are fixed film, 9,909 are suspended growth and 2,446 are classified as miscellaneous.[5] Virtually all of the treatment facilities are continuous flow although many land application systems and one suspended growth system under development are intermittent.

Suspended Growth Systems

There are many variations of the suspended growth systems currently employed for the removal of organics from municipal wastewaters. The mode of operation can dictate the net amount of organisms produced, the extent of SS degradation, the importance of intracellular materials, the settling characteristics of the organisms and the extent of treatment of priority pollutants. By varying the location of aeration, raw waste input location and organism concentration in the reactor, each of the different suspended growth systems can be made to perform, to a greater or lesser extent, in much the same way. The primary point here is that there is just one biological process and a multitude of physical variations which can be implemented. While each new physical variation is often noted as a separate process, the conversion of organics to cell mass is the primary process involved.

The physical variations of the suspended growth system may be categorized most simply as: (1) no-recycle or recycle, (2) completely mixed or plug flow, and (3) single tank or multiple tank. No-recycle systems (e.g., aerated lagoons) containing low mixed liquor suspended solids (MLSS) concentrations, require relatively large quantities of land and are found mostly in rural areas. These systems usually put out high concentrations of SS during warmer periods because of the production and discharge of non-settleable algae. The tank (actually, probably an earthen ditch) contents may or may not be completely mixed. Organisms grown may be allowed to settle either in a quiescent portion of the tank or in a separate quiescent tank. In a recycle system, the organisms grown are returned to the reactor (i.e., the OPERATOR: BIOLOGICAL REACT) so that the rate of degradation of organics can be increased and the volume of the reactor required decreased.

The generic term for a suspended growth system with recycle is Activated Sludge. The tank may either be completely mixed or channeled such that a general appearance of plug flow is achieved. Plug flow conditions are also simulated by operating several tanks in series. Depending upon the location of aeration, the application points for raw feed, the hydraulic retention time and general physical appearance, the Activated Sludge system may be referred to as Step Feed, Step Aeration, Extended Aeration, Conventional, Completely Mixed, Contact Stabilization, Oxidation Ditch or any one of a variety of other names. Those systems operated such that the organisms are first exposed to high loadings in either the inlet concentration of each in the bulk fluid. Depending upon the rate of substrate supply per unit mass of organisms present (this is often referred to as the mass loading) and the rate of aeration, the relative depth of substrate versus oxygen penetration in the floc may switch from hour to hour and from location to location within the entire reactor system. These temporal and spatial variations occur in attached growth systems as well. The extent to which these variations are allowed and controlled determines which reactions are occurring and which are responsible for overall plant behavior. As a result, two treatment plants receiving essentially the same waste and employing the same sequence of OPERATORS, may have notably different performance records.

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Process Considerations in Suspended Growth Systems

Unlike the feed streams in the chemical process industry, the INITIAL STATE for a municipal wastewater varies, virtually uncontrollably, with time. Equalization systems are sometimes used to regulate hydraulic variations. The impact of equalization on concentration changes is, however, limited. Design is further burdened by the fact that the primary components used for performance evaluation (and, therefore, design) are 5-day BOD and SS.

The 5-day BOD is a rather arbitary measure of waste strength and includes the oxygen required to convert (1) many (not all) of the soluble organics to cell mass, (2) a portion of the SS to cell mass and (3) new cell mass into carbon dioxide and water during respiration (Fig. 4). As a result, removal of 5-day BOD means little as far as specific component degradation is concerned and overlaps to a certain extent with SS. Design is clearly hindered by use of this parameter. For example, the 5-day BOD associated with the SS can conceptually be 100 percent removed in the treatment process by adsorption on the floc without any biological degradation taking place. On the other hand, SS which are adsorbed will be degraded at a rate which is notably less than that for many of the soluble components. To further complicate matters the SS can be divided into several fractions, each with its own characteristic degradation rate. The extent of degradation of the SS will depend on the time allowed for the reactions to take place.

Reactor design involves a systematic accounting of the mass of each major component entering and leaving the system. On a 24-hour basis, all components which entered the reactor and were not found in the effluent must have either accumulated in the reactor or been converted to another form. In the case of soluble BOD, the individual chemical compounds which are lumped into the non-specific BOD parameter are used as a food source by the microorganisms and converted into cell mass, carbon dioxide, water and other end products. A properly sized suspended growth system will degrade virtually all of the soluble BOD entering. A larger reactor containing a greater mass of organisms will often not appreciably reduce the mass of soluble BOD leaving the system but will convert more cell mass to carbon dioxide and water and degrade more of the incoming SS. As a result, of the two reactors receiving the same quantity of substrate and containing the same MLSS concentration, the larger reactor (having, of course, the greater mass of organisms and, therefore, lower loaded) will produce a smaller quantity of sludge provided the rate of oxygen supply is adequate.

One of the more difficult tasks in accounting for the mass of each component is the definition of the rate at which the components are degraded. In particular, the many physical variations offered as alternatives for the biological process produce confusion with respect to mixing patterns and render many of these systems virtually impossible to represent mathematically. More specifically, design formulations for systems, which are not at least completely mixed in discrete zones, are extremely difficult to develop especially when the time-varying nature of the system inputs are considered.

The rate of oxygen supply is one of the most critical factors in biological treatment. The mass of oxygen supplied each day must be equal to the mass of ultimate BOD used each day by the organisms less the oxygen equivalent of the sludge wasted each day. The oxygen equivalent of sludge can range from 1.2 kg to 1.4 kg oxygen per kg sludge. Simply stated, the more organics converted to carbon dioxide, the less sludge produced and the more oxygen utilized.

The organic portion of the sludge wasted each day is, of course, composed of unreacted SS, cell mass and cellular debris (insoluble fragments from dead portion of a tank or the first tank of a multiple tank system and then allowed to "burn-off" (i.e., oxidize) the organics in the remainder of the tank or tanks generally produce the highest quality effluent.

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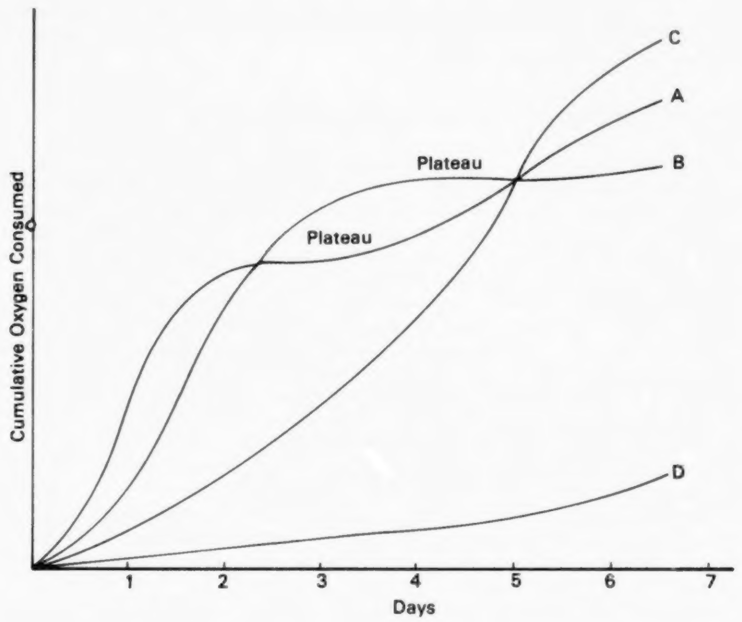


Figure 4. The 5-day BOD is an arbitrary measure.

Text for Figure 4: THE 5-DAY BOD IS AN ARBITRARY MEASURE of organic compounds. This can be readily seen in Figure 4 by considering the plot for cumulative oxygen consumed in a BOD bottle vs. time for either compound A or B. In general, all of the organics are consumed as soon as the plateau in the curve is reached. Further utilization of oxygen after the plateau results from degradation of intracellular materials (endogenous respiration), consumption of compounds released by dead organisms and respiration by higher predator forms (e.g., protozoa). As is illustrated above, the total amount of oxygen consumed in five days is identical for compounds A, B and C even though compound A had been completely removed after the second day and compound C is not fully consumed. Compound D may be considered representative of either SS or a slowly degraded organic. The standard test for BOD measurement does not provide for mixing. As a result, SS which settle during the test period may be more slowly degraded in the bottle than is possible in a mixed environment. In spite of these deficiencies, the 5-day BOD provides an excellent indication of the general strength of the wastewater and the overall performance of the treatment system. Direct use of this parameter in design, however, can lead to difficulties especially if the relative concentration of soluble and insoluble organics is not measured separately whenever either the INITIAL STATE or GOAL STATE differs from that expected for a typical municipal wastewater.

organisms). The quantity of VSS wasted each day for each kg of total 5-day BOD removed (as opposed to degraded) from the raw waste flow ranges from 0.25 to 0.85 and is often referred to as the yield of organisms. Since only a portion of the sludge wasted each day is organisms, the term cell yield does not correctly describe the mechanisms involved. The "yield" will be smallest in those systems which biologically consume the greatest quantity of oxygen (excluding nitrification) for each unit mass of total BOD removed. Lightly loaded systems with adequate oxygen supply fit well into this category. The sludge produced from these systems is usually quite stable, dewatering easily and providing few unreacted organics for methane production in an anaerobic digester. Sludges from heavily loaded systems are usually an excellent source of organics for methane production.

Current Research - Suspended Growth Systems

The discussions which follow describe observations from current research investigations. While additional studies are necessary to confirm these observations, results from many existing facilities support the concepts presented.

The adequacy of the oxygen supply system depends upon the variations in the mass loading over, say, a 24-hour period. Organisms in a suspended growth system are able to "store" organics during periods of increased load which can then be utilized during periods of reduced load. The soluble organics are "stored" internally as intracellular intermediates, nucleic acids, proteins and, perhaps, classical storage compounds such as glycogen. The SS are "stored" within the general mixed liquor mass by becoming adsorbed or enmeshed in the floc. This accumulation of organics occurs whenever the rate of organic supply to the microorganisms exceeds the rate at which oxygen is supplied for the completion of the necessary oxidative reactions (expressed, for example, in terms of the carbon dioxide production rate) (Fig. 5). As may be expected, organic accumulation will eventually result in a deterioration in effluent quality if allowed to continue until the "storage capacity" of the system is exceeded. The "storage capacity" can, of course, be exceeded in a matter of minutes or hours, depending upon the extent of reserve capacity available and the intensity and duration of an instantaneous mass load.

While organics can accumulate in the reactor whenever the dissolved oxygen (DO) concentration is above one or two milligrams per liter, the usual situation is to observe low DOs during times of accumulation and generally higher DOs during times that the oxygen supply rate is adequate. Adequacy of the oxygen supply rate depends upon both the existing loading and the quantity of "stored" organics. Proper system operation would require that the oxygen supply rate be sufficient during selected periods of a day to allow the complete oxidation of at least the intracellular organics. The extent of degradation of the "stored" SS is, of course, critical as well.

There is an intimate relationship between the operation of a biological reactor and the nature of organisms which develop in that reactor. The organisms must be able to utilize the organics and possess physical characteristics that allow easy separation (e.g., by sedimentation). For a "typical" municipal wastewater, the major organisms which develop in the system depend not only upon the average daily load, aeration supply rate and resulting DO, but also on the variations in the INITIAL STATE within a 24-hour period. This has resulted in the rather confused literature with respect to the presence and control of the poorly settling filamentous organisms. One study will cite low loading and high DO as the cause of filamentous organisms while another will cite high loading and low DO (Fig. 6). Actually, the system's ability to handle adequately "stored" organics (i.e., depending upon the match between hourly variations in load and oxygen supply rate) and not the average daily loadings and DO, will contribute significantly to both the presence and absence of filamentous organisms and, thus, the general performance of the system.

In general, the organisms that are present in a biological reactor are capable of degrading a wide variety of organic compounds. Whether or not the organism system does break down a given organic compound, however, depends upon a number of factors. For example, glucose, an organic compound readily and rapidly degradable by many of the microorganisms found in POTWs, will only be utilized by these organisms after a suitable acclimation period has elapsed. In this case, most of the organisms found in POTWs possess the genetic information for glucose degradation but do not normally synthesize the enzymatic systems necessary for the transport of glucose to the interior of the cells because glucose is not usually present in sufficient concentration in domestic wastewaters. A compound that must be present for enzyme system development and appears in the wastewater flow only periodically and/or in extremely low concentrations may not be degraded in the system. Some organisms manufacture the enzymes for degrading selected organics

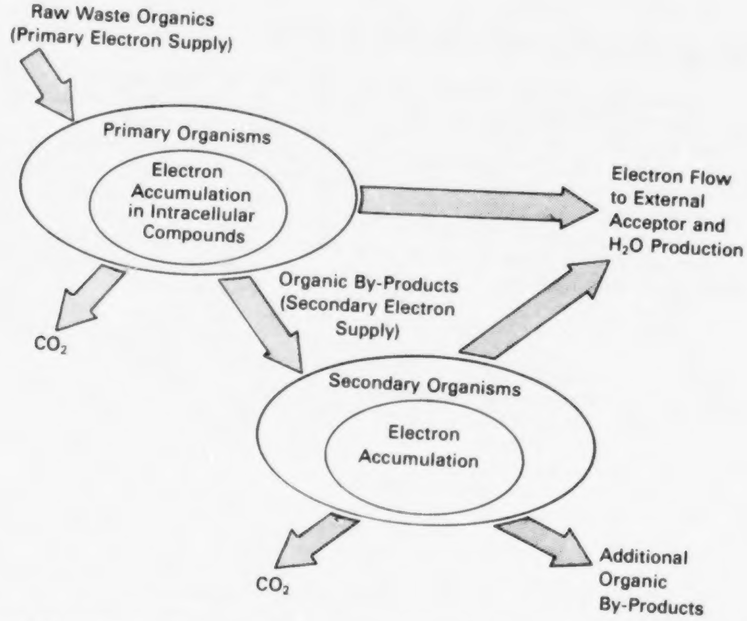
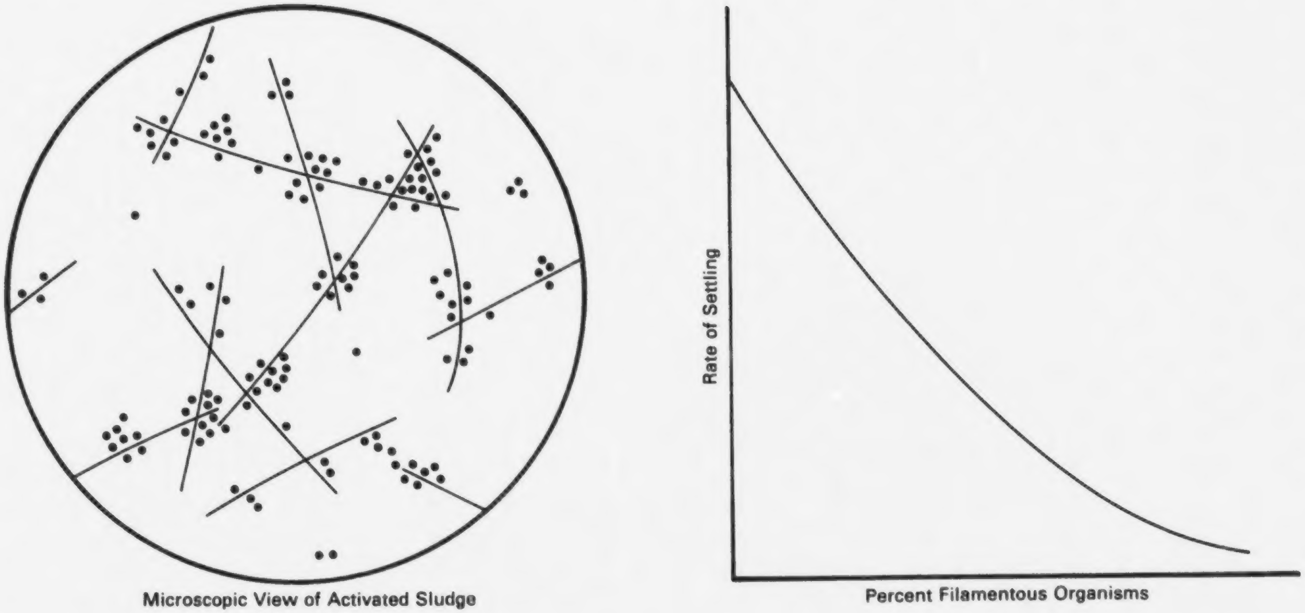

Raw Waste Organics
(Primary Electron Supply)
Primary Organisms
Electron Accumulation in Intracellular Compounds
Electron Flow to External Acceptor and H_2O Production
CO_2
Organic By-Products (Secondary Electron Supply)
Secondary Organisms
Electron Accumulation
CO_2
Additional Organic By-Products

Figure 5. The flow of electrons during biodegradation of organics.

Text for Figure 5: THE FLOW OF ELECTRONS DURING BIODEGRADATION OF ORGANICS (Figure 5) can be used to illustrate the complex interactions which take place in a biological reactor. Conceptually, electrons (organics) supplied by the untreated wastewaters may either accumulate within a primary organism system (i.e., new cell mass) or be released either to an external electron acceptor (e.g., oxygen) or in the form of organic by-products. Electrons stored in these by-products may then be utilized by a secondary organism system in the manner described above. As a result, the biological population that develops from the utilization of the same organics each day depends upon the relative importance of each of these pathways. For example, an organism system "fed" at the beginning of a 24 hour period (say, such that the external source of organics is utilized in less than four hours) will differ dramatically in character from a population that is supplied the same organics continuously and uniformly over the 24 hour period. Furthermore, a given organism may differ either physiologically or morphologically or both when subjected to one or the other feeding strategy. The intensity, frequency and duration of feeding all contribute to the selection of organisms and the definition of those reaction pathways that distinguish one organism system as a whole from another. For example, without changing the nature of the food (organics) supplied, some organism systems may accumulate and utilize storage products on a regular basis while another may generate and utilize by-products. While a change in food type would clearly complicate the analysis, the notion that a limited number of major reaction pathways dictates the performance of the system is not mitigated. Additional research must be conducted in order to determine the relative importance of these pathways in a municipal wastewater treatment plant. The mechanisms by which SS are involved must also be included.

independently of the presence of these organics. Even if the proper enzyme system is always "expressed," the rate of degradation of a given compound may be so slow that only a limited portion of that compound is utilized. Recall that, because of the slow degradation rate of SS, a lightly loaded system is generally more effective at utilizing SS than a heavily loaded system.

The only way to ensure the removal of a given component is to design the reactor such that the component of interest is reduced to the desired level. Unfortunately, many of the priority pollutants are at such low concentrations that the reactor volume required to "guarantee" biodegradation may be so large as to indicate the


Microscopic View of Activated Sludge

Rate of Settling
Percent Filamentous Organisms

Figure 6. The relative amount of filamentous organisms.

need for alternate technology. In addition, the composition of the community of organisms developed to remove the bulk of the conventional components may not perform as well as demanded in an oversized reactor (e.g., filamentous organism population may develop under lightly loaded conditions). Clearly, many of the priority pollutants, including some of those that are biodegradable, will have to be removed by non-biological methods.

Fixed Film Reactors

While approximately 63 percent of POTWs employing some form of biological treatment utilize suspended growth reactors, fixed film systems are the second most common variety of biological treatment at 21 percent.[5] Many of the comments directed at suspended growth systems apply to the fixed film systems. There is just one biological process and many physical plants to house that process. The suspended growth system is based on the premise that the microorganisms selected not only can utilize the organics supplied to the reactor but also can be separated (usually by sedimentation) from the treated wastewaters. Similarly, the fixed film system utilizes the organics, both soluble and insoluble, but selects for organisms which attach to surfaces.

The original fixed film reactors were called Trickling Filters and used rocks for organism attachment. Later systems have employed synthetic plastic media instead of rocks. In the Trickling Filters the medium remains stationary and the organics move past the medium. An alternative form of fixed film system is one in which the film is attached to a drum rotating through the wastewater flow. This system, the Rotating Biological Contactor (RBC), has received considerable attention during the past decade.

Fixed film systems as well as many land treatment applications suffer from a lack of process control alternatives which can be implemented to meet changes in either the INITIAL STATE or GOAL STATE. The primary factor responsible for this limitation is the fixed surface area for organism attachment. In a fixed film reactor, however, the fraction of the organism population which participates in the treatment can be expanded by implementing proper control strategies. For example, in a vertical column (e.g., a Trickling Filter), the relative "work" between the organisms located at the top of the column and those at the bottom can be varied by changing the hydraulic flow rate (e.g., by increasing the recirculation ratio). In addition, strategies which increase the depth of penetration of either oxygen or organics will improve the reaction potential at a given column elevation.

Text for Figure 6: THE RELATIVE AMOUNT OF FILAMENTOUS ORGANISMS present in a suspended growth reactor has a dramatic impact on the settling characteristics of the biomass. Figure 6 shows that the biological population can be thought of as being composed of discrete flocs (the dots) of non-filamentous organisms and the filaments (the lines). This is clearly an oversimplification since well over 300 species of organisms have been identified in activated sludge with more than twenty of those exhibiting filamentous growth characteristics. Nevertheless, the suggested microscopic view of Activated Sludge and the negative impact of an increasing percentage of filamentous organisms on the rate of settling are both reasonable representations of observed conditions. Suspended growth reactors are often plagued by the presence of excessive amounts of filaments. Because different filaments have different growth characteristics and nutrient requirements, a single strategy which mitigates their presence may be difficult to achieve. The literature suggests that difficulties associated with filamentous organisms can be reduced if the solids in the reactor are turned-over approximately once every three to twelve days (this is referred to either the solids detention time or the sludge age). Research currently being conducted by the author indicates that the relative fraction of filamentous organisms to the total cell mass can be controlled by regulating the extent of storage and by-product formation allowed. For example, the organism population established in a system utilizing organics in the form provided by the feed will differ from an organism population which converts the organics present in the feed into both new cells and by-products. The difference in the two populations is, of course, that the by-products represent a change in the organics available to the organisms. In a mixed culture this will result in a population shift. Other theories have been proposed. Additional research is clearly necessary.

In many cases, the organism population of a fixed film reactor can be increased only by adding support medium. Since the approximate quantity of organics consumed by a fixed mass of organisms is relatively constant in these systems, neither additional waste loads nor more restrictive effluent criteria for a given waste load can be accomodated easily. This, of course, is true of any suspended growth or fixed film biological reactor. After the apparent limit of treatment potential is reached, little can be done to extend the useful life of the facility without making a reasonably significant modification in hardware. By way of contrast, however, within certain site specific constraints, the organisms present in a suspended growth system can be increased up to two-fold during the life of the facility. Indeed, such changes can be made in a matter of days if necessary. This disparity in flexibility between fixed film and suspended growth systems was highlighted by the EPA's Office of Research and Development study[10] which noted that fixed film facilities missed GOAL STATE compliance because of deficient design practices and the suspended growth systems usually missed because of operational problems.

Current Research - Fixed Film Systems

Fixed film reactors add a dimension to wastewater treatment that must not be overlooked. It is a form of biological treatment which has served the nation's wastewater elimination problems well. Operation is relatively simple. Performance is generally consistent. Research which expands the knowledge base for fixed film reactors not only will enhance the capability of existing systems but also will allow the development of new systems which are necessary for meeting the ever escalating demands for improved performance.

Apparent limits in flexibility come, in part, from the relatively complex problems associated with theoretical descriptions of the fixed film system and the resulting lack of fundamental understanding of system operation. Theoretically sound mathematical models must include a number of factors such as (1) mechanisms of attachment of SS on the biofilm and the interference of oxygen transfer resulting from such attachment; (2) definition of liquid film thickness and the resistance to mass transfer offered by these films; and (3) definition of the active portions of the bio-film in terms of aerobic, anoxic and anaerobic reactions and rate of organic utilization in each of these zones. Results from research efforts in this area will clearly benefit the general design and operation of both fixed film and suspended growth reactors. Answers to specific questions such as those involving the impact of rotational speeds on rotating biological contactors (RBC) performance and the use of pure oxygen in closed column Trickling Filters can also be addressed.

Other fixed film systems include those in which the organisms are attached to a medium such as clay, sand or plastic. Attachment may be either on the surface or in the interior of the medium. The individual organism systems thus created may be either mixed (i.e., fluidized) or allowed to remain stationary (fixed). Such reactor configurations (especially the fluidized beds) have features of both fixed film and suspended growth facilities and are likely to have a dramatic impact on the future of biological wastewater treatment.

IMPROVING PROCESS PERFORMANCE

The fact that the newer systems are not yet facing their design loads and have not weathered the full test of time, cannot be overlooked. Nevertheless, two strategies are apparent from the development made during the seventies. First, there was an attempt to utilize oxygen more efficiently. The intricate controls instituted in the oxygen enriched systems, the fine bubble diffusers and the jet aeration systems are all examples of this attempt. Second, staged reactors, baffled areas creating discrete zones and channeled flows, allowed contact between either the return sludge or mixed liquor and elevated concentrations of organics in the raw wastewater. Virtually all of the systems designed for biological nutrient (e.g., denitrification) removal possess this feature. In general, these strategies have resulted in reduced reactor volumes, higher concentrations of organisms and lower energy consumption.

Improved efficiency of oxygen transfer will, of course, reduce costs. Perhaps more importantly, the more efficient oxygen transfer systems can respond better to changes in the oxygen demand due, for example, to increased loadings or elevated mixed liquor concentrations. This intimate relationship between tank volume and oxygen supply rate can be readily understood by considering the following example. A reactor, apparently sized twice as large as necessary but receiving oxygen at one-tenth the rate required to satisfy the organic demand, will not operate properly. Increased aerator capacity is necessary for proper operation. Clearly, many older systems receiving design loads or greater can be made to produce a higher quality effluent (without adding tankage) simply by installing more efficient oxygen transfer equipment. On the other hand, systems operated with excessive aeration relative to the organic load (as in many of the conventional Extended Aeration plants) often develop high DOs and filamentous organisms.

Improvements associated with staged reactors are more difficult to understand. Several observations, however, can be made using results from current research efforts. One is that organisms intermittently subjected to high concentrations of organics both "store" these organics and have consistently good settling characteristics. Excessive loadings can cause difficulties. Exposure to very high concentrations of organics sometimes results in the development of a turbid effluent caused by the production of dispersed organisms, even though the bulk of the organism population is associated with sludge with good settling characteristics. Another observation is that the staged reactor system evidently allows less severe constraints on the sizing of the aeration device provided that the "stored" organics are oxidized in the latter portion of the system. In particular, the DO can be essentially zero in the first portion of the system and exceed 4 mg/L or 5 mg/L in the latter stages without fostering the growth of filamentous organisms. Finally, the overall kinetics associated with soluble organic utilization (not SS) is increased in these staged systems. As a result more soluble organics can be utilized in a staged or baffled system than in a single tank reactor having the same total liquid volume. Once again the implication with regard to existing older systems is that either the useful life can be extended or the effluent quality improved by changing the reactor configuration (e.g., by adding baffles). Such a change may have to be accompanied by a modification or replacement of the existing aeration system.

Because the bulk of the research efforts and new system applications in the seventies dealt with suspended growth reactors, examples which demonstrate improved process performance for fixed film systems are less evident. One strategy, however, that has been quite successful involves the addition of a short detention time suspended growth reactor between the Trickling Filter and the final separator. Other strategies, such as increasing the recycle flow rate, have also been used to improve the performance of existing facilities.

FUTURE

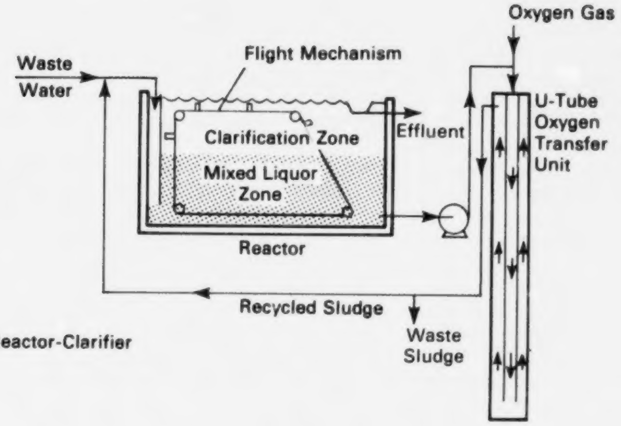
Efficiency of oxygen transfer and increased concentrations of organics (due to some form of staging) were the common features among four new treatment systems described by Barth.[illegible] These systems, the activated bio-filter,[17] the reactor-clarifier,[18] the deep shaft,[19] and the sequencing batch reactor,[20] reflect developments during the seventies for use during the eighties. The activated-bio-filter represents an obvious means for upgrading fixed film facilities which can no longer meet effluent standards. The extent of organic utilization in the fixed film portion of the system is, of course, limited by the quantity of oxygen transferred. As a result, the suspended growth reactor must be sufficiently large to complete the desired reactions. The reactor-clarifier is, from a biological process standpoint, quite similar to the activated bio-filter (Fig. 7). The initial contact of the raw waste is with oxygenated mixed liquor in a quiescent tank rather than a fixed film medium. The extent of treatment in the external U-tube used to supply oxygen to the mixed liquor relative to that in the quiescent tank used for solids separation depends upon the volumes and reaction rate of each zone.

The deep shaft employs a vigorously mixed oxygen transfer zone in the region of contact between the raw waste and the return sludge. This plus the extremely wide ranges of hydrostatic pressure experienced by the microorganisms distinguishes this system from the other two. The vigorous mixing in the zone of high loadings presumably results in a greater removal of organics in this initial contact zone than the corresponding location in either the reactor-clarifier or the activated bio-filter. Because of the rapid rate of oxygen utilization, a considerable fraction of the organics removed must be converted to carbon dioxide and water in the initial contact zone with the remaining fraction "stored" (e.g., enmeshed unreacted SS and intracellular organics) for utilization in the remainder of the shaft. Even though the loading to the deep shaft is up to five times that of conventional activated sludge plants, the yield of solids is relatively low but still consistent with the observed oxygen uptake rates. Such low yields suggest both deep penetration of oxygen into the individual flocs and a rather extensive degradation of SS. Such results point to the need to understand better the mechanisms for SS degradation.

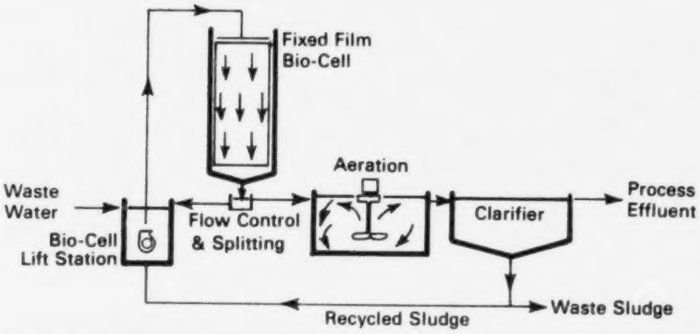
The sequencing batch reactor differs from all of the other systems discussed in that this "process" operates on a fill and draw schedule while the others are continuous flow (Fig. 8). Nevertheless, the sequencing batch reactor accomplishes in time what the continuous flow systems do in space. Perhaps the most notable difference in this system and those operated on a continuous flow basis is the flexibility offered. In a continuous flow, staged reactor system, the liquid volume in each tank is fixed and the "relative work" between any two tanks (or functions) is essentially fixed. In the sequencing batch reactor, the relative work between two functions can be adjusted as necessary by simply changing the time allotted to one or both of the functions. Four additional interesting features of the sequencing batch reactors are: (1) solids separation takes place under quiescent conditions; (2) sludge is not removed from the reaction mixture unless it is no longer necessary; (3) if properly sized, selected desired reactions such as those associated with the removal of specific priority pollutants can be allowed to go to completion after the tank is filled; and (4) short-circuiting is all but eliminated.

In order to meet changes in the GOAL STATE, such as those which may be necessitated by emphasis on organic priority pollutants, sufficient flexibility must be designed into the system to allow changes in operation. Otherwise, costly and unnecessary construction of additional facilities might be required. In addition, both the new and the old systems must be reexamined with the view to simplifying plant operation so that the personnel available for the needed jobs are not overwhelmed by sophisticated concepts and machinery. While this may seem counter to current trends, a concerted effort to accomplish this goal will generally result in improved plant performance.

On the other hand, the design engineer must seek a more fundamental understanding of the biological process. For example, if an elevated organic load followed by a period of oxidation of "stored" organics does, in fact, reduce filamentous organisms and generally improve system performance, the notion of maintaining a relatively constant load is not the best control strategy. Likewise, the benefits of periods of near zero oxygen concentration provided higher DOs can be achieved when needed should be considered in new system design and operation. More research is obviously necessary before the biological process can be understood sufficiently well for an engineer to be able to "guarantee" a design. The basic research centers presently being developed by the EPA recognize the need for answering some of the more fundamental, but yet unresolved, questions.


Oxygen Gas
Waste Water
Flight Mechanism
U-Tube Oxygen Transfer Unit
Clarification Zone
Effluent
Mixed Liquor Zone
Reactor
Recycled Sludge
Waste Sludge

(a) Reactor-Clarifier

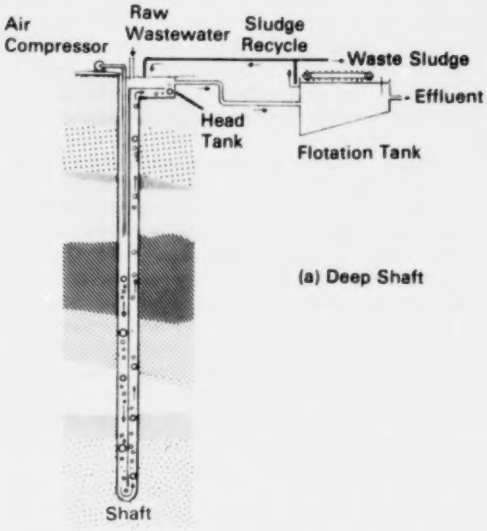

Fixed Film Bio-Cell
Aeration
Waste Water
Flow Control & Splitting
Clarifier
Process Effluent
Bio-Cell Lift Station
Recycled Sludge
Waste Sludge

(b) Activated Bio-filter

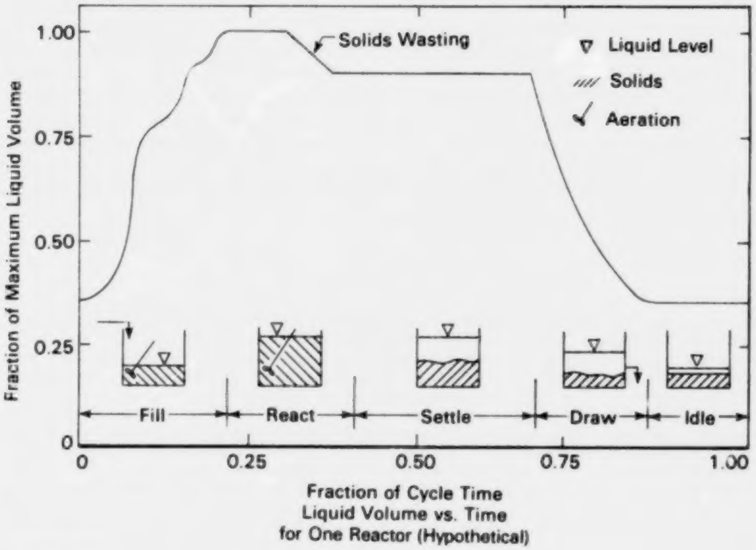
Figure 7. The reactor-clarifier and activated bio-filter.

Text for Figure 7: THE ACTIVATED BIO-FILTER AND REACTOR CLARIFIER represent variations of the biological process which possess considerable merit. Essential similarities and differences between the two systems can be seen from the schematic presented in Figure 7. The activated bio-filter is simply a combination of a Trickling Filter and an Activated Sludge system. The reactor-clarifier, on the other hand, is quite unlike most conventional treatment facilities in operation today. The U-tube oxygen transfer unit is similar to the deep shaft. Additional treatment, however, takes place in the reactor which serves as both an additional reaction zone and a secondary sedimentation tank.

As both basic research and experience from full-scale facilities become more fully bonded, mathematical models which incorporate such principles as metabolism of intracellular organics and SS utilization will be used in the design and analysis of biological reactors. At the present time, however, use of such models is quite limited for several reasons. First, many of the stoichiometric and kinetic coefficients are


Air Compressor
Raw Wastewater
Sludge Recycle
Waste Sludge
Effluent
Head Tank
Flotation Tank
Shaft

(a) Deep Shaft



(b) Sequencing Batch Reactor

Figure 8. The deep shaft and sequencing batch reactor.

difficult to evaluate and must be estimated. Second, many of the concepts are still in the early stages of development (e.g., in bio-film models) and are not generally accepted. Third, the older empirical formulations and earlier simpler models have been used successfully to design reactors which have performed adequately. Fourth, many individuals have an intuitive grasp of biological treatment which provides much if not all of that which can be obtained from the newer more sophisticated models. Finally, some individuals do not have sufficient background to allow easy understanding of many of the mathematical concepts and, as a result, are unwilling to use the new approaches.

Each of the above reasons alone is sufficient to limit use of the newer models. The combined impact is overwhelming. But intuition is not easily transferred from individual to individual. The newer systems with high organic concentrations in one zone and reduced concentrations in another force the organisms to carry out reactions which were not important in many of the older more lightly loaded reactors. As design loads for the older systems were approached and exceeded, organism behavior changed and standard operating rules were no longer sufficient. Under such conditions, the earlier models simply do not contain adequate information to allow proper analysis. Unfortunately, use of simpler models can lead to poor design and operational judgment. For example, the more complex model with estimated coefficients may (correctly) direct the designer to go to the right (figuratively speaking, of course) while the simpler model not only points to the left but also indicates how far. A better appreciation of the strengths and weakness of mathematical modeling must be developed in the eighties.

As a final note, the energy consumption associated with wastewater treatment is extremely small when compared with consumption on a national level.[21] The energy costs, however, for the operation of a given treatment facility can be quite extensive and may be responsible for heavy tax burdens to individuals located in small communities. As a result, methods for the reduction of energy requirements for existing systems are being investigated. For example, feedback DO controllers have been used to operate some systems. Because of the virtual complete use of aerobic biological systems for the treatment of municipal wastewaters, the extent to which energy utilization can be reduced in the system is somewhat limited. As a result, the EPA plans to investigate possible benefits associated with anaerobic treatment. Preliminary results with anaerobic expanded fluidized beds have been quite promising.[22] The eighties will certainly see developmental work conducted on these and other low energy anaerobic systems.

Text for Figure 8: THE DEEP SHAFT AND SEQUENCING BATCH REACTOR are depicted schematically in Figure 8. Newer versions of the deep shaft are more intricate than the one shown. Solids separation is typically achieved by flotation but sedimentation tanks have also been employed. The deep shaft is a highly loaded system which often produces a lower than expected yield of solids. The high pressures (the shafts can be as deep as 200 m) and resulting high concentrations of DO (up to 40 mg/L) may both be responsible for the low yield. The pressure changes could mechanically increase the availability of SS to the organisms. The elevated DOs may result in a positive concentration of oxygen throughout the floc. Because the rate of carbon dioxide production is increased for DOs greater than approximately 0.5 mg/L, a high concentration of oxygen through the floc would result in an increase in the overall rate of carbon dioxide production and, as a result, reduce solids yield. The sequencing batch reactor is basically a fill and draw suspended growth system. The wastewater is added to a partially full reactor containing activated sludge during a period identified as FILL. Reactions taking place during FILL are controlled by the adjusting of the mixing and aeration intensity and frequency. After the liquid level in the reactor reaches the maximum level, the wastewater is diverted (say, to another reactor) and the reactor enters a period called REACT. During REACT the required reactions are allowed to continue to completion. The extent of one reaction to another is controlled, once again by adjusting both mixing and aeration. After the desired time in REACT, all mixing and aeration provided to the reactor is discontinued so that the organisms (solids) may be separated by gravity sedimentation from the treated wastewater. This period is called SETTLE and is followed immediately by DRAW, the time during which the treated wastewater is decanted. After DRAW, the settled organisms remain in the reactor during IDLE waiting for a new supply of wastewater to be added to the reactor.

ACKNOWLEDGEMENTS

The author is extremely grateful to Mr. John Convery of the EPA Municipal Environmental Research Laboratory in Cincinnati for the time spent by him and his staff in providing source material for this chapter. In particular, special thanks should be given to B. Austin, E. Barth, R. Brenner, R. Bunch, J. Cohen, F. Evans, J. Kreissel, G. Lubin, E. Opatken, A. Petrasek, and R. Williams.

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REMOVAL OF ORGANIC SUBSTANCES FROM MUNICIPAL WASTEWATERS BY PHYSICOCHEMICAL PROCESSES

Walter J. Weber, Jr.

and

Frederick E. Bernardin, Jr.

INTRODUCTION

Physicochemical treatment (PCT) processes are generally categorized as operations which effect removal and/or destruction of undesirable organic constituents in wastewater by means other than biological degradation or conversion. In this broad context, PCT embraces a wide range of both traditional and innovative technologies.

For the present discussion, PCT processes may be defined more pertinently as technologies which practically and economically supplement or replace conventional biological treatments to yield equivalent or improved removal of organic substances. The qualifiers--practically and economically--implicitly exclude a number of processes which, although technically capable of accomplishing treatment objectives, are impracticable for one reason or another.

This chapter considers only processes which have been demonstrated on large scale--or at least proven promising on pilot scale--to be suitable for near-term application to municipal wastewater treatment. The methods reviewed include selected oxidation/conversion technologies, phase separation technologies, and

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adsorption/exchange technologies. Particular emphasis is placed on that process category which has most extensively demonstrated its feasibility for removal of dissolved organic substances; specifically, adsorption processes utilizing activated carbon.

Historic Perspectives

Several PCT processes--such as filtration and chemical coagulation--which meet criteria of practicality and economics, had already enjoyed widespread application for potable water treatment by the turn of this century. The first well-documented use of PCT technology for municipal wastewater, conversely, occurred less than 50 years ago. This application involved the chemical coagulation of municipal sewage to improve removal of suspended solids and biochemical oxygen demand (BOD); the so-called Guggenheim process.[1,2] At least part of the motivation for this development was rooted in the industrial and population expansion that had occurred during the preceding three or four decades, and in the resulting increase in pollution of receiving waters. The Guggenheim process, although technically sound, was not widely accepted in the recession and post-recession period of the 1930's, in large measure due to the higher costs associated with chemical treatment and the fact that traditional biological processes were capable of achieving extant treatment objectives relative to suspended solids and BOD.

Shortly thereafter the second world war began, and technologic developments in municipal waste treatment stagnated. In contrast, industrial growth surged in both magnitude and product sophistication. Hundreds of new synthetic chemicals were produced, largely in support of the war effort. As the nation and world emerged from armed conflict in the mid-1940's, the products of the vastly expanded industrial sector were refocused for use in agricultural and domestic applications. Concomitantly, the prosperity of the late 1940's and early 1950's encouraged major population expansions in industrialized nations.

During this period, and continuing well into the latter half of the 1950's, principal activities in the municipal wastewater field related to construction and expansion of traditional waste treatment facilities. This was aimed at achieving at least "primary" treatment (sedimentation and disinfection) for areas then discharging raw sewage, and implementation of "secondary" treatment (sedimentation plus biological oxidation and disinfection) for systems discharging to receiving waters of particular sensitivity.

In the late 1950's the federal agency responsible for both water supply and waste treatment--the Division of Water Supply and Pollution Control, U.S. Public Health Service (USPHS), Department of Health, Education and Welfare (HEW)--identified two major and convergent national problems; namely, increased water demand in the face of an essentially fixed fresh water supply and increased pollution of existing water supplies by inadequately treated waste discharges. Treatment inadequacies related both to the biologically recalcitrant nature of many of the new synthetic chemicals and to increases in volumes of sewage to be treated. Concern began to mount with respect to specific chemicals in wastewater in addition to the more traditional water quality measures of suspended solids and the oxygen demand created in receiving waters by residual biologically degradable organic substances.

In response to these problems, the Advanced Waste Treatment Research (AWTR) Program was initiated by the USPHS in the early 1960's. In July 1961 the U.S. Congress amended the Federal Water Pollution Control Act to direct the Secretary of HEW to proceed with plans to. . .

> "develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for repeated reuse."[3]

The AWTR Program, pursuant to the directives of Congress, sponsored investigation of a large number of different PCT processes. Many of these had proven successful in industrial processing and/or water treatment applications, but had not previously been applied to municipal waste treatment. This program was continued through the 1960's under the auspices of the successor water pollution control agencies, the Federal Water Pollution Control Administration (FWPCA) and the Federal Water Quality Administration (FWQA).

Conventional wisdom at the outset of the AWTR Program held that PCT processes would function best--both technically and economically--in "tertiary" mode; that is, as add-ons to secondary biological systems for advanced waste treatment (AWT), as pictured schematically in Fig. 1a. The potential of PCT processes in tertiary treatment had been demonstrated in a number of pilot-plant investigations,[4-14] and on full scale at Lake Tahoe, California,[15] and at Windhoek, South Africa.[16] In the late 1960's and early 1970's, however, several researchers began to explore the use of such processes as alternatives to biological treatment;[17-25] that is, as independent physicochemical treatment (IPCT) processes, as illustrated in the schematic diagram of Fig. 1b.

For purposes of coarse comparison, Table 1 provides approximate values for several major municipal wastewater quality parameters along with values typical of effluents from conventional, AWT, IPCT, and other treatment schemes.

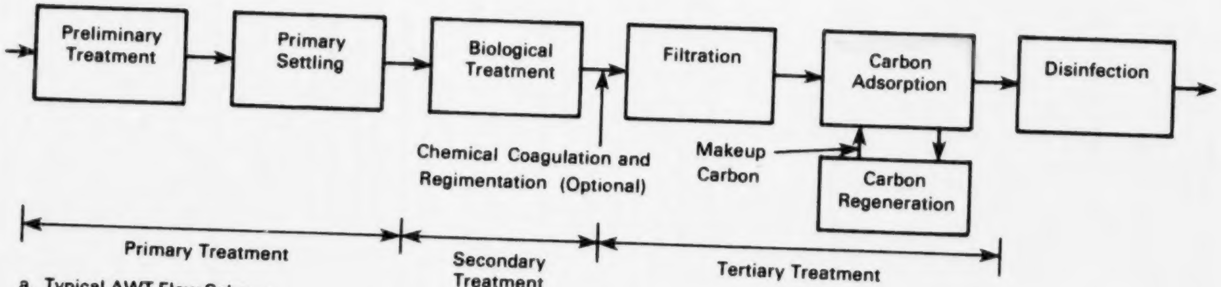
The Decade of the Seventies

The beginning of the 1970's brought both a reconsolidation of water supply and pollution control responsibilities within one agency, the U.S. Environmental Protection Agency (EPA), and a broadened enthusiasm for using both AWT and IPCT processes to accomplish higher levels of wastewater treatment and water reclamation. The EPA was instrumental in encouraging and supporting these developments. Moreover, through development and implementation of the Federal Water Pollution Control Act Amendments of 1972 (PL92-500), and subsequently the Toxic Substances Control Act of 1976 (PL94-469), the EPA implicitly redefined --more positively than had the AWTR Program before it--the principal role of PCT processes as technologies to address removal of specific undesirable compounds (e.g., toxic and carcinogenic compounds), not only BOD-producing suspended and soluble organic matter.

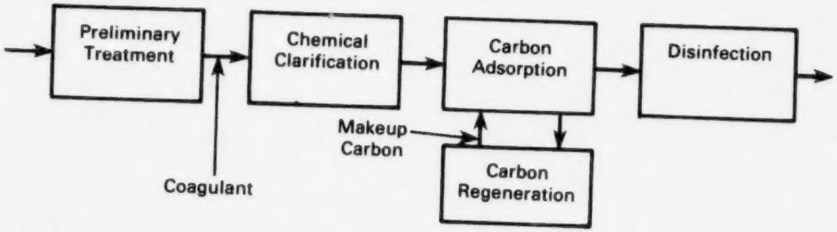
As noted earlier, the concepts and applications of the PCT processes in the tertiary or AWT mode had been well established and demonstrated on essentially full scale by the beginning of the 1970's. IPCT was yet emerging as a technology in the sense that, although firmly established in concept and pilot-plant demonstration, no full scale plants had been built and operated. The decade was destined to witness a rather remarkable transfer of IPCT technology from concept to practice. This is evident in the evolutionary progression of technical literature on the subject.

The IPCT literature of the early 1970's relative to municipal waste treatment is concerned primarily with bench-scale tests, pilot-plant demonstrations, and preliminary design developments. The mid-1970 literature presents reports on the final design details and start-up activities of IPCT plants. By the close of the decade the literature emphasis had shifted toward evaluation of the performance characteristics, operational aspects, and economics of operating IPCT processes.

Concurrent with these large-scale engineering applications and evaluations, notable progress was made in the 1970's toward mechanistic definition of process variables operative in PCT processes, and toward the translation of these findings into mathematical models to facilitate computer-aided design and operation. It is worth noting that, while many text and reference books relating to biological treatment process concepts and design had been available for several preceding decades, it was not until 1972 that the first text devoted to PCT technologies appeared.[26]


Preliminary Treatment
Primary Settling
Biological Treatment
Filtration
Carbon Adsorption
Disinfection
Chemical Coagulation and Regimentation (Optional)
Makeup Carbon
Carbon Regeneration
Primary Treatment
Secondary Treatment
Tertiary Treatment

a. Typical AWT Flow Scheme


Preliminary Treatment
Chemical Clarification
Carbon Adsorption
Disinfection
Coagulant
Makeup Carbon
Carbon Regeneration

b. Typical IPCT Flow Scheme

Figure 1. Applications of activated carbon in municipal wastewater treatment.

Table 1. Approximate Performance Characteristics of Different Municipal Wastewater Treatment Processes

		Process Effluent Characteristics						
Parameter	Influent Waste	Primary	Primary with Chemical Addition	Conventional Secondary	PAC/ Chemical	PACT*	IPCT	AWT
BOD, (mg/L)	300	150	75	35	15	5	8	1
COD, (mg/L)	480	240	130	50	35	40	30	10
SS, (mg/L)	230	100	20	25	20	15	4	1
Turbidity, (Jackson turbidity units)	250	150	12	50	10	20	2	0.5
PO_4, mg/L	12	9	2	6	2	5	1	0.5
Color, (chloroplatinate color units)	Highly variable	Highly variable	50	50	15	20	10	7

*PACT, powdered activated carbon treatment, is a patented process (E.I. du Pont de Nemours and Co.) in which powdered carbon is added to the aeration basins of otherwise conventional biological secondary treatment plants.

PCT processes for municipal wastewater have thus progressed rapidly in a relatively short period. During the 1960's PCT was brought from conceptual design to successful pilot and small scale demonstration. The decade of the 1970's witnessed emergence of such technology from pilot stage to design of plants with capacities as large as 100 million gallons per day (MGD), and start-up and operation of a number of plants utilizing different designs to implement essentially similar unit processes. Experience with the operating and performance characteristics of the variety of designs of the 1970's is serving to bring PCT processes through the complete evaluation cycle, and to establish a firmer basis for future selection and engineering design of such processes based on proven relative economic and technical merits. The pioneering research and applications engineering of the 1970's will in the 1980's serve to optimize PCT process configurations and ancillary equipment, and to refine this technology for use in municipal wastewater treatment. The work of the 1970's will also contribute much valuable information with respect to the use of PCT processes for related applications in industrial wastewater and potable water treatment.

OVERVIEW OF PHYSICOCHEMICAL TREATMENT PROCESSES

PCT processes may function to modify or degrade chemical structures to form less undesirable species or to separate these substances from solution for subsequent disposal or destruction. Several processes that have demonstrated reasonable suitability for municipal applications are briefly reviewed herein. One major distinction and advantage such processes share in common over biological treatments is the degree of operational control which they afford. PCT processes generally can be designed to accomplish any degree of removal desired, thereby facilitating the tailoring of cost-effective treatment systems for specific applications.

It was noted at the outset of this chapter that PCT processes function primarily by non-biologic means. The degree to which the term "non-biologic" accurately describes the function of a PCT process may vary considerably from one application to another. With biologically active fluids such as municipal wastewaters, competing, interfering or synergistic biological interactions are virtually assured. Detailed discussion of the specific ways in which microorganisms can affect the performance of PCT processes is beyond the scope of this overview. The topic will be considered briefly in a subsequent section of the chapter as it relates to the most widely used class of PCT processes--activated carbon adsorption.

Degradation Processes

Degradation reactions entail modification or conversion of substances by changing their oxidation states. The purpose of such treatment is to convert undesirable chemical species to species which are neither harmful nor otherwise objectionable. This is accomplished in some instances by use of chemical agents, and in other instances by application of heat or some other form of non-chemical energy.

Oxygen,[27] ozone,[28-30] permanganate,[31] chlorine dioxide[32] and chlorine[33,34] have all been examined as reagents for direct chemical degradation processes in a variety of water and industrial waste treatment contexts, but only on a very limited basis for municipal waste treatment. Other strong oxidizing agents such as hydrogen peroxide[35] and potassium ferrate[36] have received even less attention for a number of reasons, including considerations such as handling, stability, and cost. Advances during the late 1970's in the technology of production, handling and applications of such reagents, particularly hydrogen peroxide are likely to enhance future feasibility of use.[37]

Several "indirect" degradation processes have shown promise. A number of studies, for example, have demonstrated the feasibility of induced oxidation by short-lived radicals generated during treatment of wastes with ultraviolet (UV) irradiation.[38] The combined use of ozone and UV irradiation has also proven effective for oxidation of certain wastewater constituents.[39]

The direct and indirect degradation processes cited above have had limited application for municipal wastewater treatment. They are included in this brief overview largely on the basis of promise demonstrated on laboratory scale or in applications to industrial water treatment. Thermal degradation processes, conversely, such as wet-air oxidation[40] and incineration[41,42] have had comparatively wide-scale use in municipal applications. Such processes can provide for nearly complete destruction of many organic waste constituents, and have particular advantages for treatment of high-strength, low-volume waste streams such as municipal sludges. It must be recognized, however, that extremely high temperatures and relatively long retention times are required for effective destruction of certain priority pollutants, such as polychlorinated biphenyls (PCBs). Further, careful consideration must be given to the fact that a number of toxic compounds are readily volatilized in thermal degradation processes, and may thus create potential air pollution hazards.

Separation Processes

Separation technologies of interest in the context of organics removal from municipal wastes include:

(1) coagulation/sedimentation;
(2) filtration;
(3) membrane processes; and
(4) adsorption processes.

The first two of the above process categories principally--but not exclusively--address separation of suspended particulate organic matter. State-of-the-art technology for these two categories of processes was conveniently summarized in a design manual published by the EPA in 1971.[43] The membrane and adsorption process categories include operations designed--again principally but not exclusively--for removal of dissolved impurities. The following paragraphs provide a brief discussion of significant developments that took place during the 1970's relative to all four categories of separation processes.

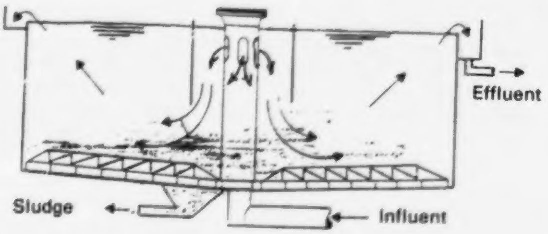
Coagulation/Sedimentation—

These operations are probably the best understood and most widely employed of all PCT separation technologies in municipal waste treatment applications. They are frequently used as pretreatments to reduce the operational difficulties that high concentrations of particulate and colloidal material may otherwise pose for subsequent operations such as filtration, adsorption, and disinfection. Fig. 2 illustrates typical clarifier units for settling solids after chemicals have been added to promote their coagulation and aggregation into settleable entities.

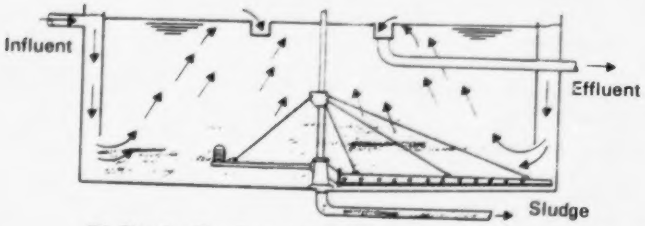
Emphasis in the area of coagulation/sedimentation during the decade of the seventies focused largely on the chemical enhancement of the aggregation-settling characteristics of sewage solids by addition of inorganic (e.g., ferric chloride, calcium oxide, aluminum sulfate) and synthetic organic polyelectrolyte coagulants and coagulant aids. Removals as high as 70% for BOD and 90% for suspended solids were reported achievable for raw sewage.[44-46] Other significant studies by the EPA compared the relative performance characteristics of various coagulants on a broader scale.[47] In related equipment developments, tube settlers and inclined plate clarifiers, the concept of which is illustrated in Fig. 3, were investigated[48] for their potential advantages over more traditional sedimentation basin configurations.

Filtration—

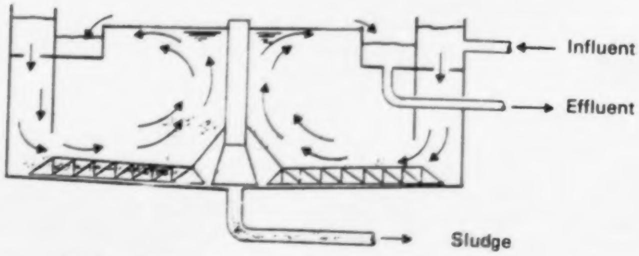
There was recognition during this period that filtration processes--used widely for potable water treatment--could function effectively for removal of non-settleable



(a) Circular Center-Feed Clarifier with
a Scraper Sludge Removal System



(b) Circular Rim-Feed. Center Take-off Clarifier with a
Hydraulic Suction Sludge Removal System

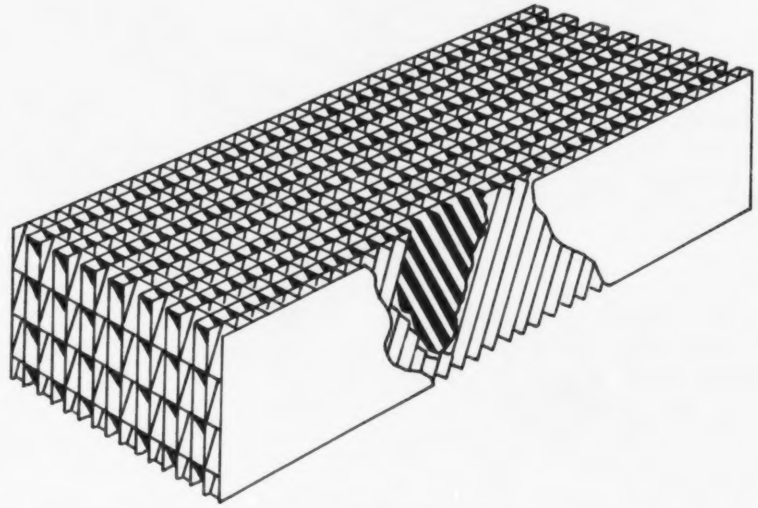


(c) Circular Rim-Feed. Rim Take-off Clarifier

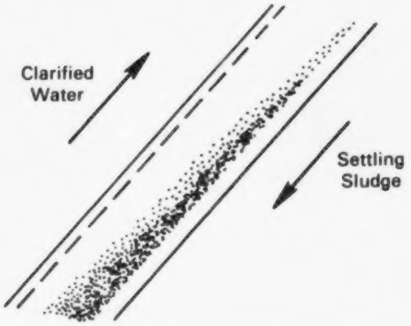
Figure 2. Typical clarifier configurations (From Reference 43).

suspended and colloidal organic matter from municipal wastes. Early indications that filtration could play a major role in upgrading effluent quality spurred activity in the research, development, design, and evaluation of wastewater filtration processes.

Filtration of waters and wastes has been carried out in a variety of configurations, including pre-coat filtration, low-rate and high-rate deep-bed filtration, and microstraining.[26,43,49,50] The most common and successful configuration has been of high-rate filtration through a bed of granular media such as sand, coal, or activated carbon. Such filtration is usually carried out in open beds which operate under the gravitational influence of a static head of water over the bed. Pressure filtration in closed vessels is an alternative design used more frequently for industrial waste



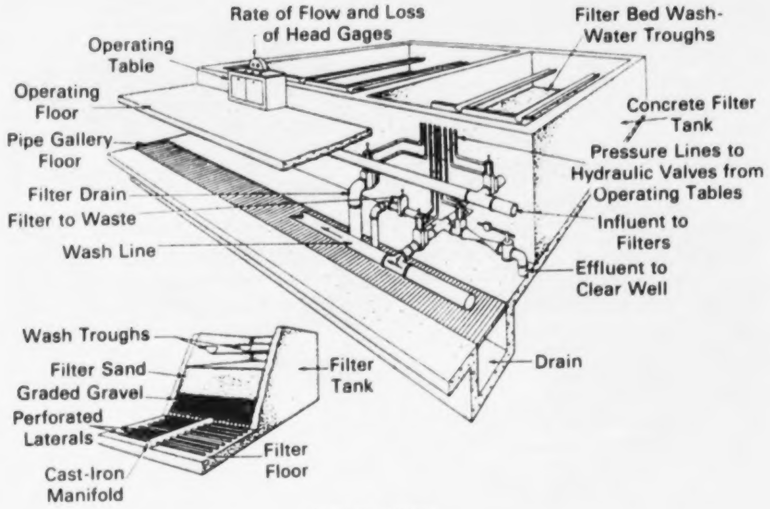
Modular Unit of Inclined Settling Tubes.
(Courtesy of Neptune Microfloc, Inc.)



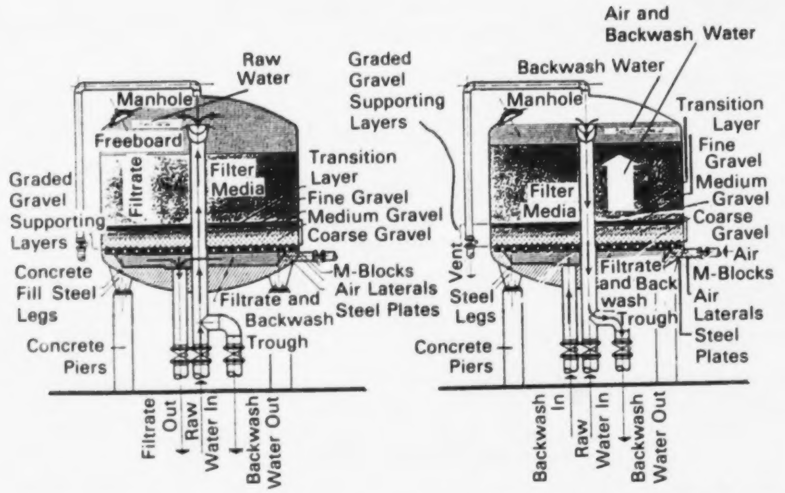
Flow of Liquid and Sludge in Steeply Inclined Tubes.
Counter Flow of Water and Sludge in Single Tube.

Figure 3. Tube-settlers for sedimentation (From Reference 43).

treatment than in municipal systems. Pictorial representations of open-bed and pressure filters are given in Fig. 4. In either system excessive accumulation of solids in or on the media eventually restricts flow and causes backpressure. At this point the solids are removed by upward-flow or backwash fluidization of the bed. Backwashing is commonly augmented by a mechanical or hydraulic surface wash.[51] Additionally, it is desirable to inject air at the bottom of the filter to increase physical contact and scouring of the filtration media, thereby improving release of the accumulated waste solids during backwash.


Rate of Flow and Loss of Head Gages
Filter Bed Wash-Water Troughs
Operating Table
Operating Floor
Concrete Filter Tank
Pipe Gallery Floor
Pressure Lines to Hydraulic Valves from Operating Tables
Filter Drain
Filter to Waste
Influent to Filters
Wash Line
Effluent to Clear Well
Wash Troughs
Filter Sand
Graded Gravel
Perforated Laterals
Cast-Iron Manifold
Filter Tank
Filter Floor
Drain

Gravity Filter


Raw Water
Manhole
Freeboard
Filtrate
Filter Media
Graded Gravel Supporting Layers
Transition Layer
Fine Gravel
Medium Gravel
Coarse Gravel
Concrete Fill Steel Legs
M-Blocks
Air Laterals
Steel Plates
Filtrate and Backwash Trough
Concrete Piers
Filtrate Out
Raw Water In
Backwash Water Out
Air and Backwash Water
Backwash Water
Graded Gravel Supporting Layers
Manhole
Transition Layer
Fine Gravel
Medium Gravel
Coarse Gravel
Filter Media
Vent
Air
M-Blocks
Air Laterals
Steel Plates
Steel Legs
Filtrate and Back wash Trough
Concrete Piers
Backwash In
Raw Water In
Backwash Water Out

Pressure Filter-Filter Cycle Schematic

Pressure Filter-Backwash Cycle Schematic

Figure 4. Filtration systems (from Environmental Pollution Control Alternatives: Municipal Wastewater, USEPA Technology Transfer, EPA-625/5-76-012).

Filtration performance is significantly dependent upon the nature of the solids (i.e., inorganic or organic, gelatinous or discrete), the type of filter and media used, pretreatment practices (including the use of coagulants as filter aids), and the frequency and efficiency of backwashing. Reports of filtration efficiencies of 90% or more have been published, with 50% to 80% removal being typical. Effective filtration can commonly reduce effluent suspended solids levels to below 10 mg/L, thus producing water ideally suited for further treatment to remove dissovled organic materials or, in some cases, suitable for direct discharge or limited reuse.

Membrane Processes—

Requirements for removal of supra-colloidal and dissolved organic and inorganic impurities in AWT systems spurred interest during the 1970's in membrane separation processes; actual applications, however, were limited. The two major membrane processes for removal of organic substances, ultrafiltration (UF) and reverse osmosis (RO), utilize applied pressure as a driving force for separation of impurities from water, as depicted in Fig. 5. The membranes employed for UF have much larger pore sizes than those used for RO, and the pressures involved are correspondingly lower. Because of the large membrane pore sizes involved, UF is used primarily to separate fine particulate, colloidal, and macromolecular organic matter, while RO is employed principally for removal of dissolved substances.

Ultrafiltration, which can produce high quality water with respect to suspended solids, has been employed in a few cases for direct filtration of biologically treated fluids to replace sedimentation and improve quality.[52,53] The largest and most pertinent application of RO for municipal waste treatment has been as a component in an AWT system producing water for reuse in the recharging of ground water supplies.[54]

Adsorption Processes—

Adsorption emerged in the early years of the 1970's as the most generally applicable separation technology for removal of dissolved organic pollutants from municipal wastewater, and was strongly promoted as such by the EPA.[55,56] Activated carbon has demonstrated effectiveness for a broad range of organic pollutants and is the adsorbent of choice for most wastewater applications. The process of adsorption is depicted conceptually in Fig. 6.

The ability of activated carbon to remove dissolved organic material from solution has been long known. Before the 1970's, however, full-scale application of this technology had been limited largely to industrial operations--in which the cost of the carbon system could readily be justified--and to use for taste and odor control in potable water treatment. Detailed considerations regarding these applications are given in companion chapters in this Monograph by O'Brien et al.[57] on industrial wastes and by DiGiano[58] on municipal water supplies.

Taste and odor compounds are usually present in low concentrations in water supplies, and often the need to provide removal occurs only periodically. Consequently, the common mode of activated carbon application in water treatment was one in which an appropriate quantity of carbon was introduced to a given volume of water, held in contact with the water for a specified period, then separated and discarded. The form of carbon used for such operations was usually powdered, largely for reasons of lower initial cost, adaptability to intermittent operation, and ease of removal by existing sedimentation and filtration processes.

This mode of operation was, logically, one of the first attempted for wastewater treatment, but it did not prove entirely satisfactory. The relatively larger amounts of organic impurities present in municipal wastes and the need for continuous treatment in this application required more efficient utilization of the activated carbon. Further, the fact that large amounts of carbon are needed for such operations requires a scheme of regeneration and reuse of the carbon. These requirements suggested the desirability of using granular activated carbon (GAC) in continuous contacting systems.

The potential of adsorption for tertiary treatment of wastewaters was well demonstrated during the mid-to-late 1960's in several pilot and large-scale PCT projects. By the beginning of the 1970's, IPCT had been developed and successfully demonstrated at the pilot-scale as an alternative to biological treatment for direct

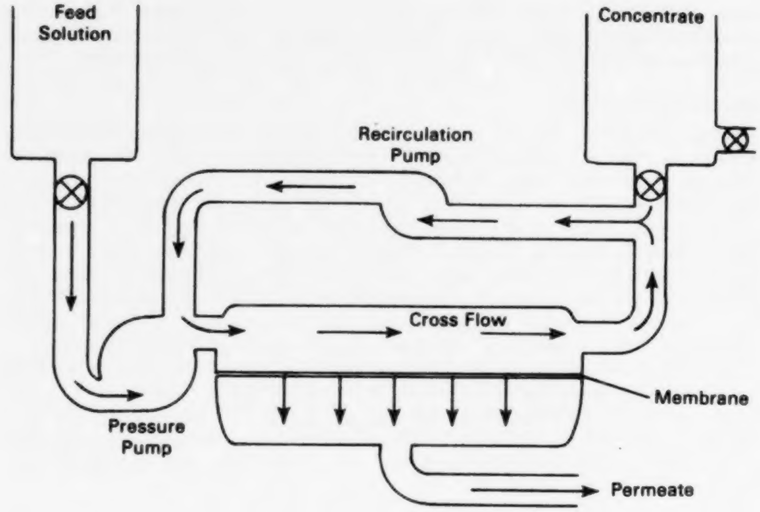

Feed Solution
Concentrate
Recirculation Pump
Cross Flow
Membrane
Pressure Pump
Permeate

Figure 5. Schematic representation of a membrane process using pressure as a driving force for separation (from Gregor, H.P. and C.D. Gregor, "Synthetic Membrane Technology *Scientific American*, July 1978).

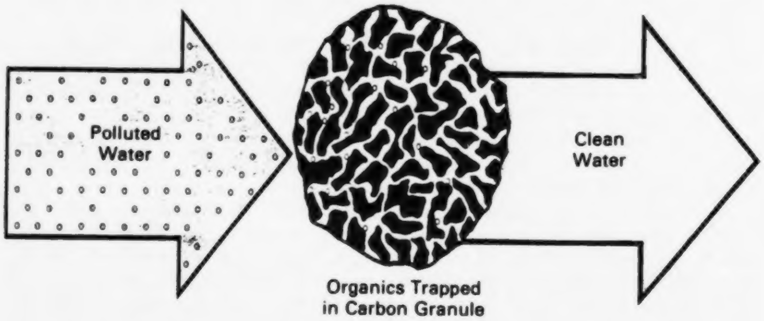

Polluted Water
Clean Water
Organics Trapped in Carbon Granule

Figure 6. Conceptual depiction of the adsorption process (Courtesy of Calgon Corp).

application to raw wastewaters. In this early work the basic IPCT process scheme consisted of chemical coagulation and sedimentation followed by GAC adsorption beds. In a number of cases, granular media filtration preceded the GAC.

Data from pilot operations and small-scale plants incorporating GAC operations indicated consistent organic matter removals of 95% or more despite variations in waste strength and composition. Toxic substances, which would have adversely affected biological treatment processes, appeared to have little or no effect on the IPCT process. The effluents produced by those early pilot plants were reported to be essentially free of suspended solids and to contain only about 5mg/L to 10mg/L of total organic carbon (TOC) and BOD. IPCT processes utilizing inorganic coagulants were further reported to achieve generally high degrees (~95%) of phosphate removal. This resulted in IPCT processes--specifically including GAC--being advanced by the EPA in 1973 as the most sophisticated and complete treatment systems available.[59]

In addition to possessing superior adsorptive properties for a broad range of dissolved organic substances, GAC exhibits favorable filtration capabilities. This characteristic further broadened the usefulness of GAC in municipal waste treatment. It was used as media for both filtration and adsorption in a single reactor, and backwashed, cleaned, and handled in a manner similar to that used for more conventional granular filtration media. Its use as a dual-function medium prompted a number of detailed studies on specific pretreatment requirements for various operating modes.[47,60,61]

Granular activated carbon can be transferred hydraulically, and requires no special handling or storage conditions. The fact that GAC can be regenerated effectively by thermal means is a key to its successful economic application, and was a prime factor in opening the field of municipal waste treatment to adsorption technology in general, and to GAC in particular.

Comparisons of activated carbon and alternative adsorbents--particularly synthetic resins--have shown carbon to be much more suitable for municipal wastewater treatment due to its applicability to the wide range of organics present.[62-66] For this reason, as well as costs, synthetic resins received little attention during the decade of the seventies in municipal wastewater treatment. For only a limited number of industrial waste treatment applications and certain by-product recoveries have carbonized polymeric adsorbents and macroporous cross-lined polystyrene and polyacrylic ester adsorbents been effective alternatives to activated carbon.

Biological growth on GAC has been found to be a natural consequence of applying this high-activity material to municipal waste treatment.[19,23,67,68] Such growth has been variously reported as deleterious and advantageous. The use of appropriately designed and operated integrated systems, in which biological growth on the surface of granular activated carbon is properly controlled, has been shown to provide a favorable combination of adsorption and biodegradation in single reactors.[69-72]

The most promising use of powdered carbons for municipal waste treatment has been in integrated systems in which the carbon is added to the aeration basins of activated sludge plants and/or to anaerobic digesters to upgrade the performance of these systems and enhance removal of toxic materials.[73-75]

Overview Summary

A wide range of different types of PCT processes was evaluated for potential AWT and IPCT applications during the 1970's. Of these, adsorption on activated carbon, frequently preceded by coagulation/sedimentation and/or filtration, was clearly shown to be the most suitable process for achieving high levels of removal of organic compounds from municipal wastewaters. The remainder of this chapter expands upon the concepts of this process, significant design and operational features, and discusses its specific AWT and IPCT applications.

ADSORPTION AND ACTIVATED CARBON TECHNOLOGY

Principles of Adsorption

The phenomenon of adsorption is of major significance in most physical, chemical and even biological water and wastewater treatment operations. In his chapter of this Monograph, DiGiano[58] provides a thorough and comprehensive summary and analysis of significant developments which occurred during the 1960's and 1970's relative to adsorption principles in aqueous systems. These will not be recounted here. It is of complementary value, however, to set forth a conspectus of state-of-the-art knowledge with respect to variables which significantly impact the effectiveness and efficiency of activated carbon adsorption operations in wastewater treatment.

Fundamentally, adsorption involves the concentration of soluble and quasi-soluble impurities from solution at an interface or surface. The material concentrated is termed the adsorbate; the material at whose surface the concentration occurs is termed the adsorbent. Fig. 7 depicts the distribution of an organic molecule between solution phase and a solid surface. For each combination of a specific type of organic substance, solution conditions, and type of surface, a quantitative equilibrium distribution between solution and surface phase is defined; several such distributions are illustrated in Fig. 7. The character of this distribution markedly affects the feasibility of adsorption for a particular application. It, in turn, is influenced by a variety of factors. Prime among these for a specific application is the nature of the adsorbent. As noted earlier in this chapter, activated carbon has been demonstrated to be the most effective adsorbent for water and wastewater treatment applications.

Properties of Activated Carbon

The generic term "activated carbon" encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive associated surface areas. The large surfaces are formed by selective burning and oxidation of the raw material during activation, creating a microporous end product. Fig. 8 characterizes the physical form of a granule of activated carbon, illustrating the extensive intraparticle pore structure. The large surface area of this material derives from surfaces associated with the near-molecular size pores and capillaries within the carbon granules.

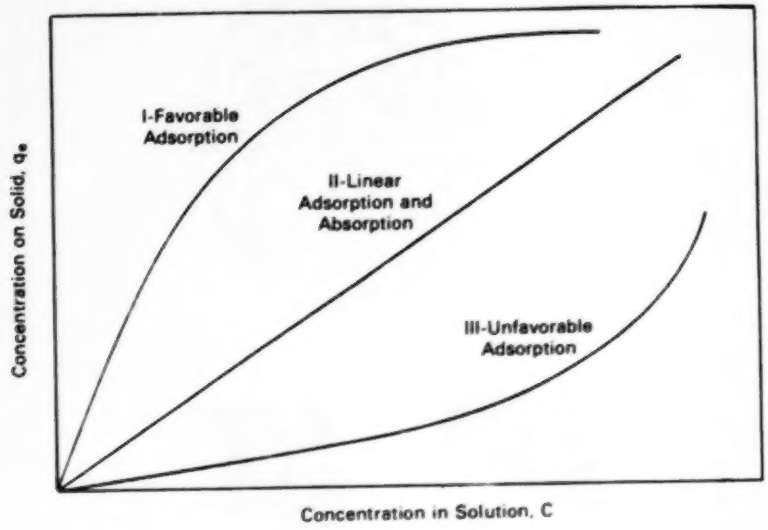
Commercial carbons typically have total surface areas in the range from 450 m^2/g to 1500 m^2/g. This extensive internal surface area is theoretically available for adsorption of organic compounds from wastewater. The actual surface area available is, however, dependent on the specific nature of the organic adsorbate, and can be considerably less than the total. The pore volume of these carbons ranges from 0.5 cc/g to 1.5 cc/g. It is, however, only that fraction of the total pore volume which is contained in larger pores (>10 Å) which determines, to a significant extent, the effective capacity of carbons for liquid phase applications. The effective capacity thus depends on the distribution of area or volume with pore size, and the distribution of molecular sizes to be adsorbed.

The surface properties of activated carbon are additionally important in determining activity; that is, capacity for adsorption of a specific organic substance. The chemical properties of the surface depend on the raw material used, the type of activation process, and the conditions employed in activation. Activated carbon surfaces can be considered to consist of essentially two different types. Planar, non-polar surfaces comprise the bulk of the surface for most carbons. Heterogeneous edges of the carbon planes, which make up the microcrystallites whereon carbon-oxygen functional groups formed by oxidation in the manufacturing process are located, constitute the second type of surface. The groups attached to these surfaces enable activated carbon to undergo halogenation, hydrogenation, oxidation, and to function as a specific adsorbent and catalyst in a variety of different reactions.

Although it does not directly affect adsorption capacity, the hardness or durability of individual granule structures is a most important property to be considered in carbon selection, at least for GAC applications. This property largely determines the losses which will occur on each adsorption-regeneration cycle as a result of attrition during handling and burn-off during reactivation. Petroleum, lignite and bituminous coal-based carbons are typically used in GAC systems, while softer wood and peat-based materials find more use as powdered carbons.

Pressure drop or head loss in downflow columns and bed expansion in upflow columns of GAC are determined in part by particle size distribution. These

(a) Graphical Representation of Types of Adsorption Separations



(b) Typical equations for description of solid/liquid phase distributions

The Langmuir Equation:

$$q_e = \frac{Q^\circ bC}{(1 + bC)}$$

where Q° represents the ultimate capacity and b the relative energy (intensity) of adsorption

Two convenient linear forms of the equation are

$$\frac{C}{q_e} = \frac{1}{bQ^\circ} + \frac{C}{Q^\circ}$$

or

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \left(\frac{1}{bQ^\circ}\right)\left(\frac{1}{C}\right)$$

The Freundlich Equation:

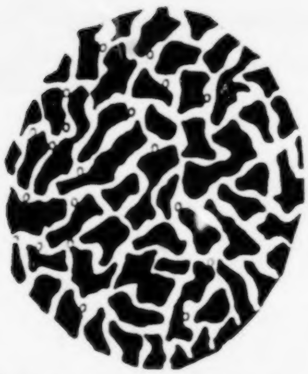
$$q_e = K_F C^{1/n}$$

where K_F is a measure of limiting capacity and n the relative energy (intensity) of adsorption

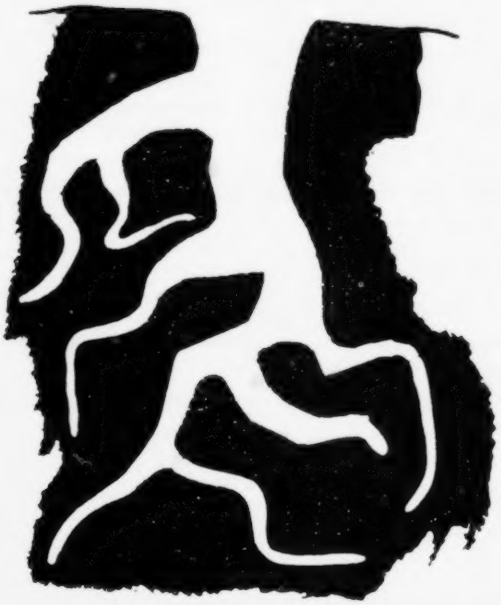
In linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C$$

Figure 7. Distribution of an organic substance between solid and liquid phases (after Weber, Reference 26).



Cross Section of a Granule of GAC



Cross Section of Pore within Granule

Figure 8. Conceptual drawing of carbon granule (Courtesy of Calgon Corp).

properties, in turn, influence design, installation and capital costs. The smallest size particle that conditions of efficient operation permit generally should be used, for this increases adsorption rates, and thus reduces the size of the adsorption system required.

The general properties of some commercially available GACs and PACs are given in Tables 2a and 2b, respectively.

Table 2a. Properties of Selected Commercial Granular Carbons

Properties	CALGON Filtrasorb 300	WESTVACO WV-L	ICI AMERICAS Hydrodarco 3000	CARBORUNDUM GAC-30	WITCO 517
Raw material	Bituminous coal	Bituminous coal	Lignite coal	Sub-bituminous coal	Petroleum
Surface area, (m^2/g)	900-1000	1000-1050	550-650	900-1000	1050
Mesh size, U.S. Std.	8 × 30	8 × 30	8 × 30	8 × 30	12 × 30
Density					
Apparent, (g/cc)	0.50	0.48	0.43	0.51	0.52
Backwashed, Drained, (lb/ft^3)	27	25-27	23	28	30
Effective size (mm)	0.8-0.9	0.85-1.0	0.8-0.9	0.85	0.89
Uniformity coefficient	<1.9	<1.8	<1.9	<2.1	1.4
Ash content, (%)	<10	<10	<18	<15	<0.5
Iodine no., (mg/g)	>950	>950	>550	>900	>1000
Abrasion no. (Ro-Tap)	>70	>70	-	>70	>85
Moisture, (%)	<2.0	<2.0	<9.0	<2.0	<1.0
Mean particle diameter, (mm)	1.5-1.7	1.4-1.7	1.4-1.6	1.5-1.7	1.2

Table 2b. Properties of Selected Commercial Powdered Activated Carbons

	ICI AMERICAS HYDRODARCO C	WESTVACO NUCHAR SA-15	CALGON TYPE RC
Properties			
Raw material	Lignite coal	Wood	Bituminous coal
Surface area, (m²/g)	550	1400-1800	1100-1300
Particle size, (% less than 325 mesh)	70 (min)	65-85	65-75
pH	10.5	3-6	-
Density			
Apparent, (g/cc)	-	0.40	0.48
Tamped, (g/cc)	0.70	-	-

Adsorption on Activated Carbon

Adsorption of organic compounds from water by activated carbon results from a variety of binding forces between organic molecules and the carbon surface, all having their origin in electromagnetic interactions. Two principal types of adsorption are commonly distinguished; i.e., physical and chemical.

Physical adsorption derives from the action of van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic forces. Chemical adsorption results from the reaction of an adsorbate with an adsorbent, commonly resulting in a transformation of the chemical form of the adsorbate. The resulting chemisorptive bond is localized at active centers on the adsorbent and is usually stronger than that derived from the physical van der Waals forces.

Adsorptive interactions between organic molecules and activated carbon also result from specific but non-transformative interactions between solute molecules and functional groups on the adsorbent surface. These interactions, designated "specific adsorptions," may exhibit a broad range of binding energies, from values commonly associated with physical adsorption to the higher energies usually involved in chemisorption.

The net dispersion, electrostatic, chemisorptive, and functional-group interactions broadly constitute a category of adsorptive reactions relating to the affinity of the carbon surface for specific organic compounds. The extent of adsorption may also be predicated on various interaction characteristics of these compounds with water itself, notably those of surface tension and solubility.

Many organic compounds of interest for waste treatment can effectively alter the surface tension of water. The energy balance of aqueous systems of such compounds favors their adsorptive concentration at the carbon-water interface. The extent of adsorption is greatly influenced by the degree of insolubility or hydrophobicity of the organic compound; that is, its degree of "dislike" for water. Increasing hydrophobicity generally increases the extent of adsorption. The effects of solubility can be interpreted in terms of the necessity of breaking a form of bond between an organic compound and water before adsorption can occur. The greater the solubility of the compound, the stronger the bond, and the smaller the extent of adsorption.

A number of parameters specific to a given system will thus contribute to the adsorption of organic compounds by activated carbon in wastewater treatment applications. These include--relative to the organic substances--concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration, and the nature of background or competitive organic substances. Temperature and pH can also markedly influence adsorption performance to the extent that they can effect changes in the aforementioned parameters.

Rates of adsorption are also highly important. The more rapid the approach to the particular equilibrium distribution dictated by the above factors, the greater is the fraction of equilibrium capacity utilized in a given time of contact between the carbon and the wastewater being treated. There are essentially two consecutive rate-limiting mass transport steps in the adsorption of organic compounds from wastewater by activated carbon, as illustrated schematically in Fig. 9. The first of these is the transport of the compound through a surface film to the exterior of the carbon (film diffusion). The second is the diffusion of the compound within the pores of the carbon and/or along pore-wall surfaces (intra-particle diffusion). A significant amount of research on adsorption technology during the 1970's focused on development of mechanistic interpretations regarding--and mathematical models for description of--the time-variable dynamics of adsorption of organic molecules from aqueous solution by activated carbon. Such information is essential for evolution of rigorous and optimum criteria for adsorber--or reactor--design and operation, and for identification and control of important system variables.

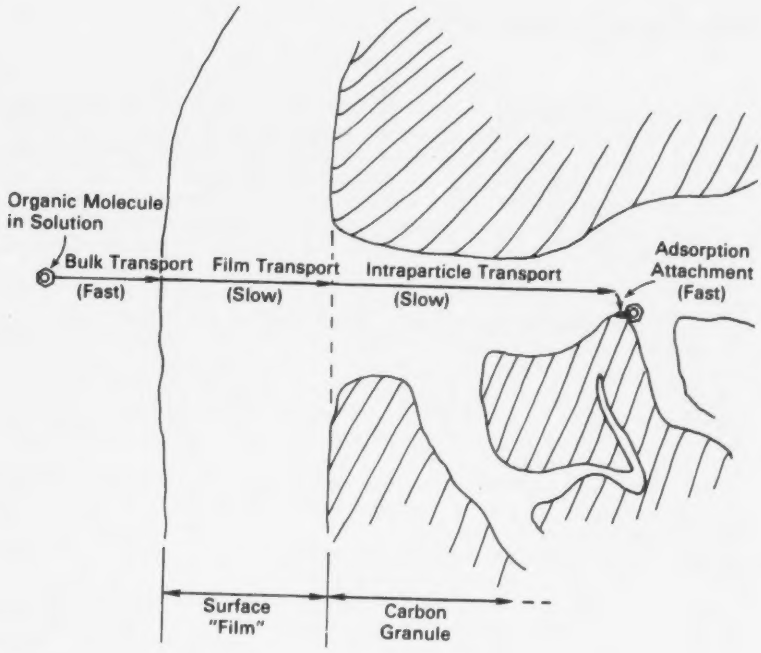


Figure 9. Significant mass transport steps in adsorption.

Reactor Systems

The manner in which to contact carbon most effectively with a wastewater is of particular significance for large scale treatment operations. As noted, rates of adsorption on carbon depend significantly on the particle size of the carbon. It is desirable, therefore, to employ carbon of as small a diameter as conditions of efficient operation permit. The qualification "efficient operation" is key, for the size of particle chosen dictates to some extent the type of reactor system. Powdered carbon, for example, is generally used in either a completely mixed batch (CMB) or completely mixed flow (CMF) reactor, both of which are pictured schematically in Fig. 10. Head loss using PAC through a bed or column reactor would be prohibitive. For granular carbon, on the other hand, suspension in a batch reactor would be difficult, while a plug-flow (PF) column or fixed-bed operation, the principle of which is illustrated in Fig. 11, is efficient.

Continuous-flow operations have advantages over batch-type operations because rates of adsorption depend upon the concentration of organic matter in the wastewater. Plug-flow, or column reactors have advantages over CMF reactors for the same reason. In column operations the carbon at the inlet of the bed is continuously in contact with the concentrated influent waste. The concentration in the water in contact with a given layer of carbon in a column changes very slowly under this condition, and high uptake levels of adsorbate by the adsorbent are achieved. For batch treatment, conversely, the concentration of organic substance in contact with the entire quantity of carbon continuously decreases as adsorption proceeds, thereby decreasing the effectiveness of the carbon for removing the organic material. These considerations, coupled with the difficulty associated with

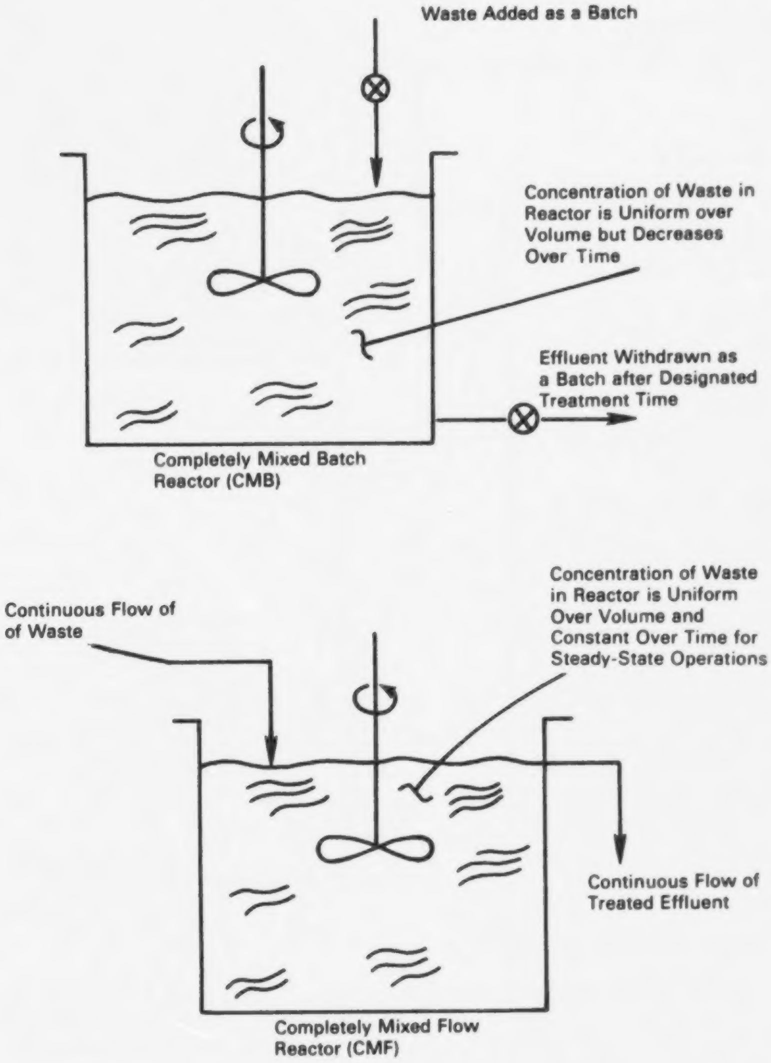

Waste Added as a Batch
Concentration of Waste in Reactor is Uniform over Volume but Decreases Over Time
Effluent Withdrawn as a Batch after Designated Treatment Time
Completely Mixed Batch Reactor (CMB)
Continuous Flow of of Waste
Concentration of Waste in Reactor is Uniform Over Volume and Constant Over Time for Steady-State Operations
Continuous Flow of Treated Effluent
Completely Mixed Flow Reactor (CMF)

Figure 10. Completely mixed reactors.

regeneration of powdered carbon, have made granular carbon the choice for most of the large scale continuous wastewater treatment operations built during the 1970's.

Fig. 12 illustrates several arrangements and reactor configurations typically used for GAC systems. There are two basic PF modes of conduct for column adsorbers relating to exhaustion/regeneration of the carbon; namely, fixed beds and pulsed beds. In the fixed-bed mode an entire GAC bed is removed from service when the carbon is to be reactivated. In the pulsed bed, only the most exhausted portion of the

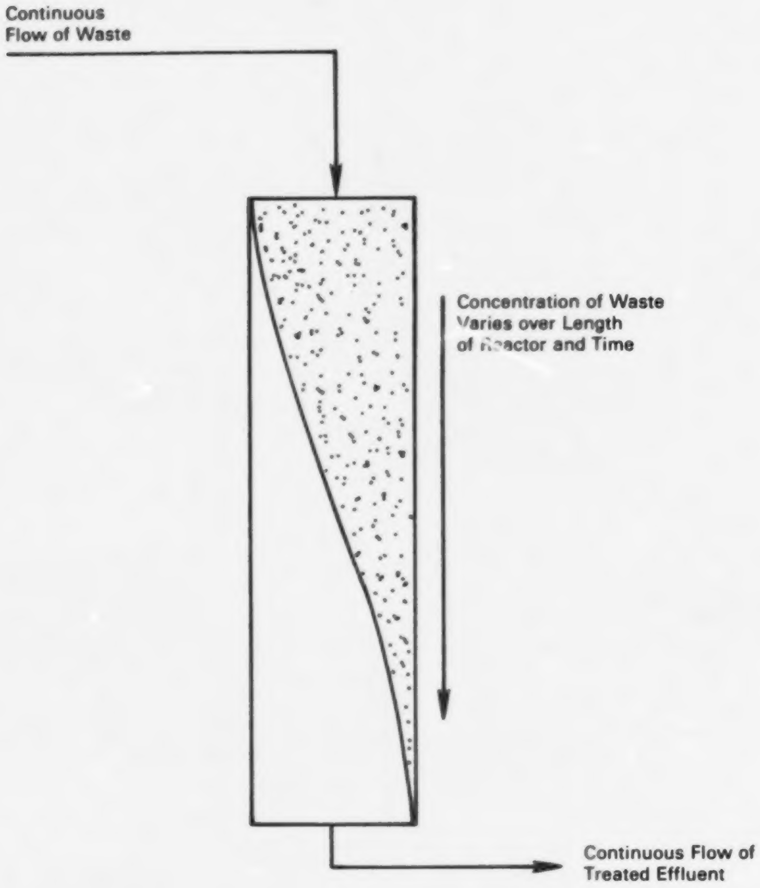
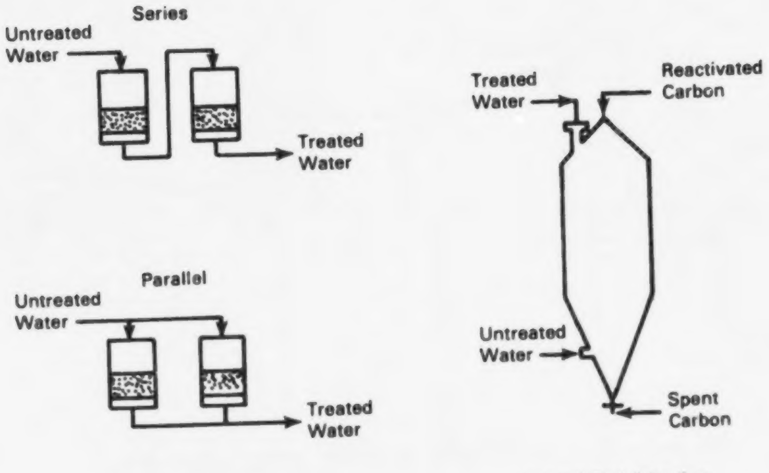


Figure 11. Plug-flow reactor.

total bed is removed as an increment of new carbon is added simultaneously. For the relatively low organic content of municipal wastewaters, the increased efficiency of pulsed bed operation is not worth the additional capital cost for equipment; fixed-bed systems predominate in this application.

Within the fixed-bed mode of conduct, adsorption beds may be operated in series or parallel. In the series system, the effluent from the first bed passes to a second, then, if necessary, to additional beds in series. The advantage gained by this mode of operation is that the carbon in the lead bed can be exhausted more fully--and, therefore, used more cost-effectively--in achieving a desired system effluent concentration than can the carbon in a single larger bed of size equal to the sum of the sizes of the smaller beds in series. In a series operation the lead bed is removed for reactivation when it is exhausted. The next bed in sequence then assumes the lead position and a fresh bed is added in the final position. The most common series-type system for municipal waste treatment is comprised of two operating beds with a third on standby.



Fixed-Bed Systems

Pulsed-Bed Adsorber

Figure 12. Typical GAC reactor configurations.

In parallel fixed-bed operations the effluent of all columns is blended prior to discharge. This provides the potential advantage of ensuring that the average concentration of the total effluent flow meets discharge criteria although the effluent from any one bed or more may exceed these criteria. The adsorption beds are removed from operation for reactivation in a staggered manner, so that the system is comprised of beds in varying states of exhaustion. This type of system is very common for municipal waste treatment.

The adsorption beds of both series and parallel design can be operated in either an upflow or downflow direction. A downflow mode of operation must be used where the GAC is relied upon to perform the dual role of adsorption and filtration. Although lower capital costs can be realized by eliminating pretreatment filters, more efficient and frequent backwashing of the adsorbers is required. Filtration rates of 8.2 cm/min to 40.7 cm/min (2 to 10 gallons per minute per square ft., gpm/ft^2) are employed, and backwash rates of 48.9 cm/min to 81.5 cm/min (12 to 20 gpm/ft^2) are required to achieve bed expansions of 20% to 50%.

Alternatively, adsorption beds have been designed and operated in the upflow mode. While prefiltration is normally required, excessive head loss, channeling, and fouling of the GAC can be avoided by upflow operation. In addition, smaller particle sizes of GAC can be employed to increase adsorption rate and decrease adsorber size. In attempts to combine the best of both these modes of operation, systems have been designed to operate in an upflow-downflow series mode.[76]

When wastewater is passed through a stationary bed, for either upflow or downflow adsorption operations, non-steady-state conditions prevail in that the carbon continues to adsorb steadily increasing amounts of organic matter over the entire period of useful operation. Fig. 13 is a plot of an idealized adsorption pattern or breakthrough curve for such a non-steady-state adsorber. The "breakpoint" on this curve is that point at which the effluent from the adsorber no longer meets treatment objectives, dictating disposal and/or regeneration of the GAC contained in the bed.

Factors which affect the actual shape of the breakthrough curve include the adsorbate concentration, pH, rate-limiting mechanism for adsorption, nature of the equilibrium conditions, particle size, depth of the column or bed, and the velocity of

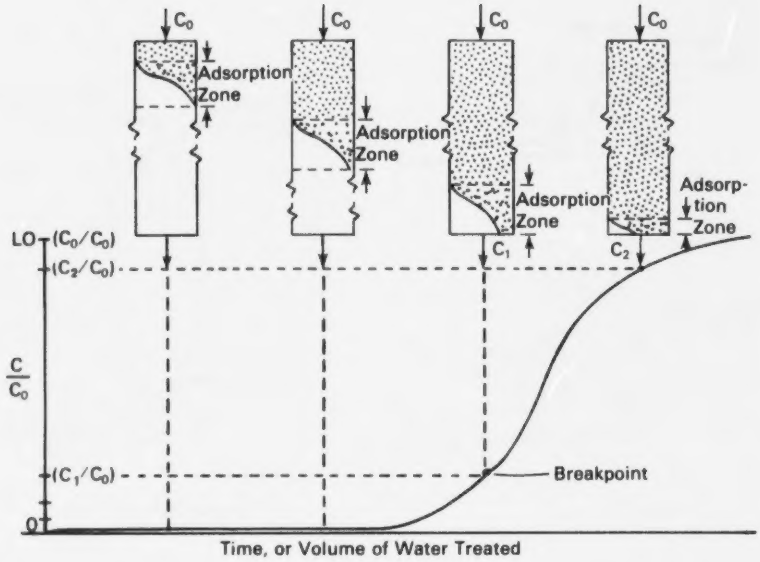


Figure 13. Idealized breakthrough curve (after Weber, Reference 26).

flow. In general, the time to breakpoint for a specific type of carbon and given organic substance is decreased by: (1) increased particle size of the carbon; (2) increased concentration of organic matter in the wastewater; (3) increased pH of the wastewater; (4) increased flow rate; and (5) decreased bed depth.

Adsorber Modeling and Design

The design of fixed-bed adsorbers involves estimation of the shape of the breakthrough curve and the appearance of the breakpoint. A substantial amount of the time and expense in planning and designing adsorption facilities is involved in predicting or forecasting the operational dynamics of the process for a given application. This generally requires extensive experimental pilot studies. The duration and costs for such pilot studies frequently can be minimized by mathematic models which are capable of the required prediction and forecasting given certain basic information about the system of interest.

Considerable development work relating to predictive models for adsorption system design was initiated in the late 1960's and continued throughout the 1970's.[26,65,66,70,77-92] It is beyond the scope of this chapter to discuss all of these modeling procedures in detail. To present some perspective, however, it is of value to consider briefly the Michigan Adsorption Design and Applications Model (MADAM).[65,66,70,83,87-89] This model is based on numeric solution techniques, and not restricted to over-simplified rate and/or equilibrium expressions to facilitate mathematic solution. It can accommodate the dynamic aspects of fluid dispersion, solids mixing, multi-solute interactions, and--importantly, as noted in the next section--biological growth on activated carbon surfaces, aspects which must be excluded because of mathematic complexity from models which are based on analytic solution techniques.

The MADAM algorithms enable predictive modeling of fixed-bed adsorption operation; i.e., prediction of concentration breakthrough profiles for various adsorbents, column configurations, hydrodynamic conditions, types of solutes and operational conditions. An example of actual fixed-bed data and corresponding predicted breakthrough curves for *p*-chlorophenol and several different adsorbents are depicted in Fig. 14. Fig. 15 illustrates the MADAM predicted breakthrough profile and measured data for adsorption of dodecyl benzene sulfonate from an aqueous mixture of this organic compound and phenol.

It is clear from these figures that reasonable predictions can be made of the behavior of fixed-bed adsorption systems with respect to individual organic substances, both in "pure" solutions and in simple mixtures, through the use of appropriate mathematical models. Such models have also been used with reasonable success to predict breakthrough of lumped measures of organic material (e.g., BOD, COD, TOC), and further work is in progress to adapt them to predictions of the adsorption behavior of individual components in highly complex mixtures.

Bioactive Carbon Systems

Biological activity in activated carbon beds used for wastewater treatment is to be expected. Municipal wastewaters are bioactive by nature, and the surfaces of activated carbon provide excellent sites for colonization by microorganisms.[69-72,93-95] The adsorptive properties of activated carbon serve to enrich substrate and oxygen concentrations, the surface provides recesses that are sheltered from fluid shear forces, and the variety of functional groups on the surface can enhance attachment of microorganisms. It has been clearly demonstrated that activated carbon provides a more effective surface for growth of attached organisms than do inert media such as sand and non-activated coal materials.[69-72]

Fig. 16 is a scanning electron microscope (SEM) photograph of a carbon granule taken from a waste treatment application. The prolific growth of microorganisms on the surfaces of the granule may be readily observed. The SEM photo clearly demonstrates an ecosystem including bacteria and bacteriovorous protozoans. The micrograph also demonstrates that the biofilm is not uniform, but is comprised of a permeable matrix.

Bioactivity has been variously reported as advantageous and disadvantageous to the primary adsorptive function of the carbon. The depth and composition of the biofilm may influence adsorption dynamics if it is extensive enough to block pore openings or to retard boundary layer transport processes.

There have been speculations that biological activity serves to "regenerate" activated carbon. Bioregeneration, per se, is not likely, since most bioforms are too large to enter those pore spaces which contain the majority of the effective adsorption area. It has been demonstrated that, under proper conditions of design and operation, biological activity can improve removal of certain types of waste contaminants and can prolong periods between required replacement or regeneration of the carbon.[68-72,93-95] This, however, likely relates more to reduction of the effective loading on the carbon--as a result of the biodegradation of a certain percentage of the organic compounds within interstitial void spaces and at the external and macropore surfaces of carbon granules--than it does to bioregeneration via degradation of substances which have already been adsorbed within the internal meso and micropore structure of the carbon.

Preoxygenation and/or pretreatment with other oxidants, particularly ozone, can enhance bioactivity in carbon beds.[96-99] This enhancement relates in part to oxidative conversion of organic matter to more readily biodegradable forms, and in part to enriched levels of oxygen in the bed. It is important to note that preoxidative treatment with ozone is not likely to enhance adsorption reactions, as was suggested in a few literature reports during the 1970's. Indeed, such pretreatment is more likely to convert aromatic compounds to oxygen-rich polar aliphatic substances, which are not as well adsorbed by activated carbon as are the less polar aromatic precursor compounds.

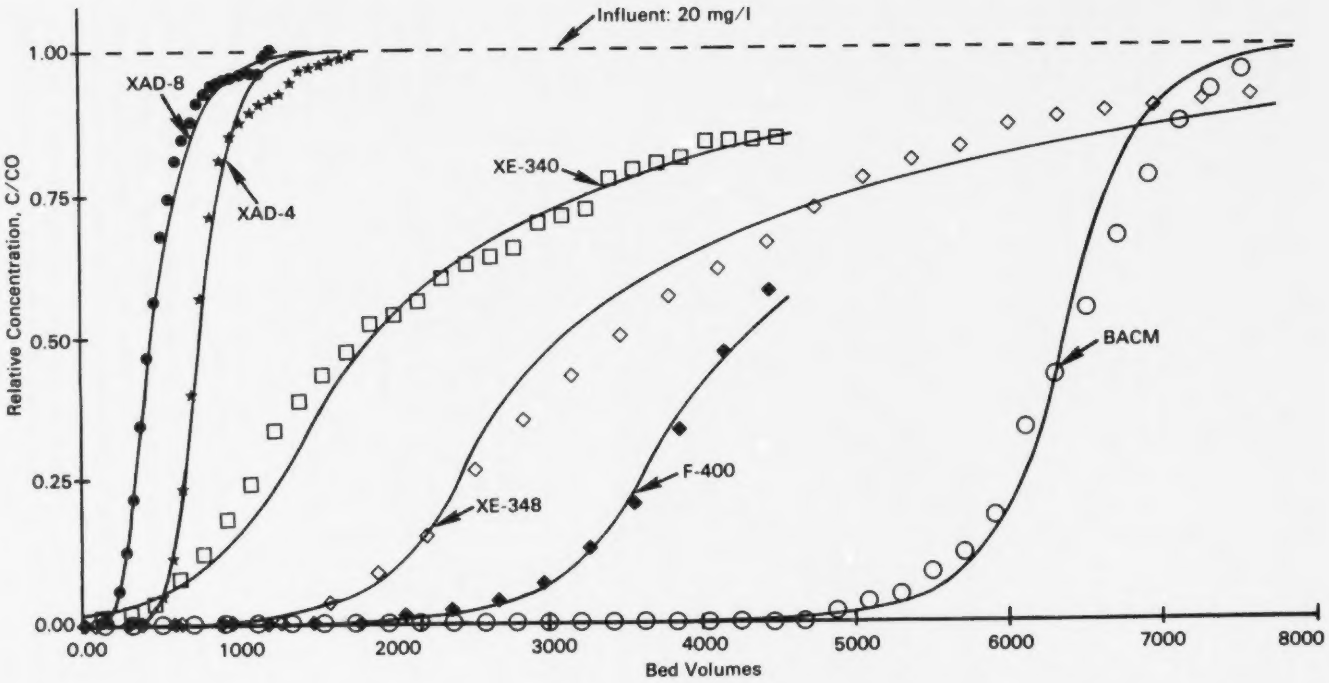


Figure 14. Adsorber breakthrough curves for p-chlorophenol and various adsorbents. The symbols denote experimental data, and solid lines represent predicted profiles (After Van Vliet and Weber, Reference 65).

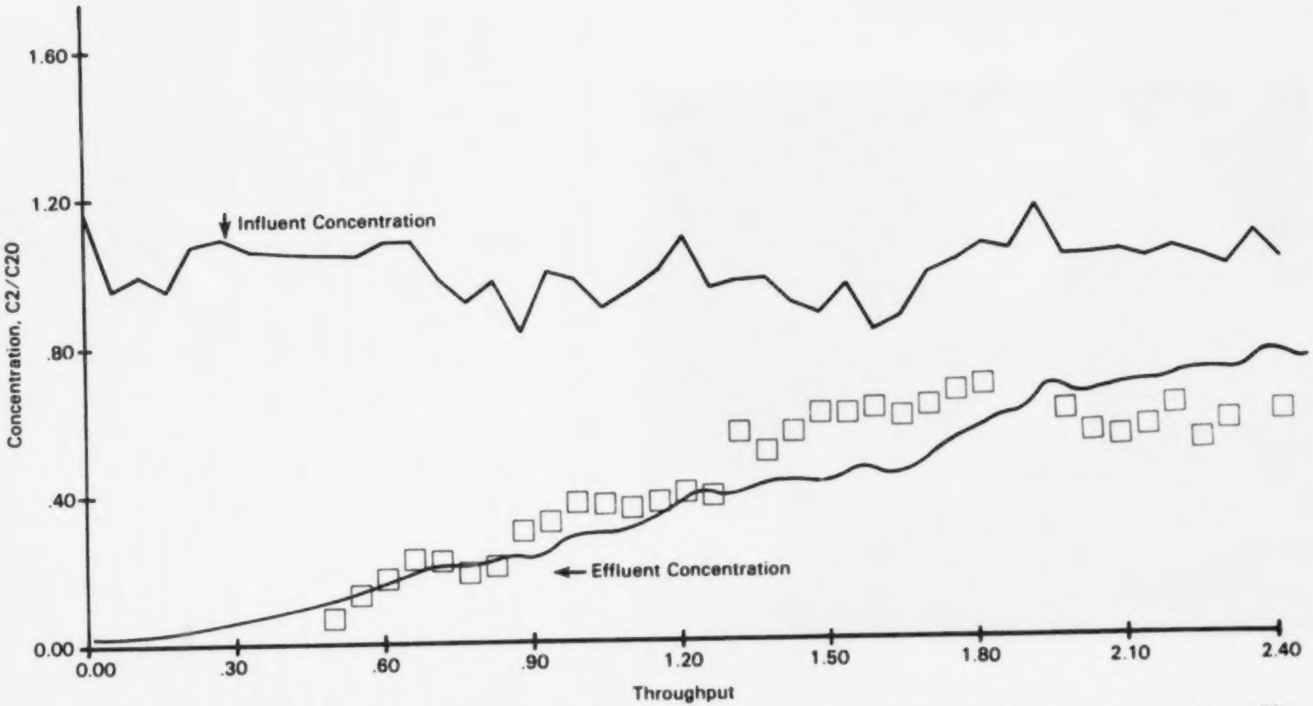


Figure 15. Dodecyl benzene sulfonate influent and effluent concentration (C2/C20) profiles; phenol – dodecyl benzene sulfonate mixture (After Crittenden and Weber, Reference 89).

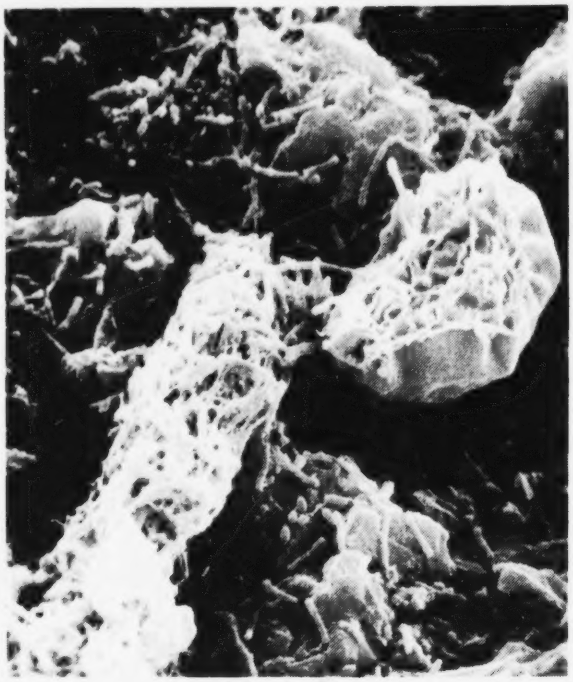


Figure 16. A scanning electron microscope picture of carbon surface with attached microoroganisms (After Weber, et al., Reference 94).

As noted earlier, bacteria are too large to significantly penetrate the pore spaces of activated carbon. Thus, development of a biofilm should present no additional resistance to internal, or intraparticle, diffusion. Because the biofilm is on the outside of the carbon particle, substantial resistance to transport of substances controlled primarily by external, or "film," diffusion should be anticipated. It is possible to minimize the additional external resistance by providing operating conditions which ensure that the biofilm is maintained as a thin, active film which is not allowed to cover the entire external surface of the carbon. Regular and vigorous air scouring to maintain a thin active biological film has been found essential to minimize the resistance of the biofilm to transport of adsorbing substances, minimize adverse effects on the primary function of the activated carbon, and to control head loss in the adsorber.[60,61,69,70]

In further attempts to utilize observed synergistic interactions of activated carbon adsorption and biological oxidation, investigators at E.I. DuPont in Deepwater, NJ performed extensive studies on the effects of adding powdered activated carbon to activated sludge systems.[73-75] In the PACT® * process, which resulted from this work, virgin or reactivated carbon is added to settled wastewater entering a conventional activated sludge aeration tank in order to improve the performance of the biological system. The quantity of carbon added is related to the type of contaminant to be removed, the degree of removal to be achieved, and to the sludge age or sludge retention time (factors related to the extent of recycle of biomass and carbon solids in the system). The economic application of this technology to organic removal in municipal wastewater treatment requires a viable means for regeneration of the PAC. Reactivation of PAC in a conventional multi-hearth furnace presents a number of difficulties, although it has been successfully accomplished.[100-102] The first full-scale municipal system using PACT®, however, was designed to provide both excess sludge destruction and PAC regeneration through a wet air oxidation process;[103,104] this system is illustrated in Fig. 17.

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*PACT ® is a registered service mark of E.I. DuPont de Nemours & Co., Inc.

Because activated carbon has strong tendencies to adsorb oxygen from solution,[105] PAC surfaces can provide both sites of attachment for organisms and sites of enriched oxygen concentrations in activated sludge systems. In most applications, the increased biomass and carbon solids associated with PACT® can be accommodated in existing equipment, allowing higher loadings and/or improved performance. The ability of activated carbon to adsorb toxic organic and inorganic materials is an advantage in stabilizing activated sludge operations where spills or spikes of toxicants are experienced.[106] Further, excursions in influent concentrations of biodegradable organics can be attenuated by PAC, thereby reducing the adverse effects of shock loadings to the system. Finally, increases in sludge weight and density resulting from the presence of PAC assist the separation of the mixed liquor suspended solids from the treated water.

While further research is needed for a full understanding of integrated biological-PCT processes, it is obvious that such systems have substantial potential for improving organic removal in municipal waste treatment in the next decade. This is particularly true for PAC-activated sludge systems because of the economic benefits to be realized by using existing facilities.

Reactivation and Regeneration

Economic large-scale application of activated carbon, particularly GAC, generally requires its repeated reuse. This in turn requires periodic restoration of the adsorptive properties of exhausted carbon, by either reactivation or regeneration. For this discussion, the term "reactivation" refers to a process in which such restoration is accomplished using conditions similar to those involved in the production or activation of the carbon, while "regeneration" connotes the use of processes other than those employed for initial activation. Several methods are available to accomplish reactivation and/or regeneration. These include chemical, solvent extraction, and thermal techniques.

Chemical regeneration makes use of changes in adsorbability which accompany chemical changes in adsorbed molecules. An illustrative example is phenol which is adsorbed well at neutral and low pH conditions. At high pH, however, the phenol molecule is converted to the phenolate ion, which is only weakly adsorbed. Therefore it is possible to design treatment systems to remove phenol from solution at neutral or low pH and regenerate the carbon and recover the phenolate under basic pH conditions.[107]

For easily volatilized adsorbed compounds, such as benzene, hot gases or steam can be used to convert the adsorbed material to gaseous form and to strip this form of the adsorbate from the carbon.

Solvent regeneration makes use of differences in the solubility of certain compounds in water and in other solvents. An adsorbate with a high affinity for carbon and/or low solubility in water can be adsorbed effectively from aqueous phase. Draining the exhausted adsorbent bed of water and contacting it with a solvent, such as alcohol, in which the adsorbate is highly soluble will result in desorption of the substance and regeneration of the carbon. A final steaming can be used to clear the bed of the volatile solvent and prepare it for another adsorption cycle.

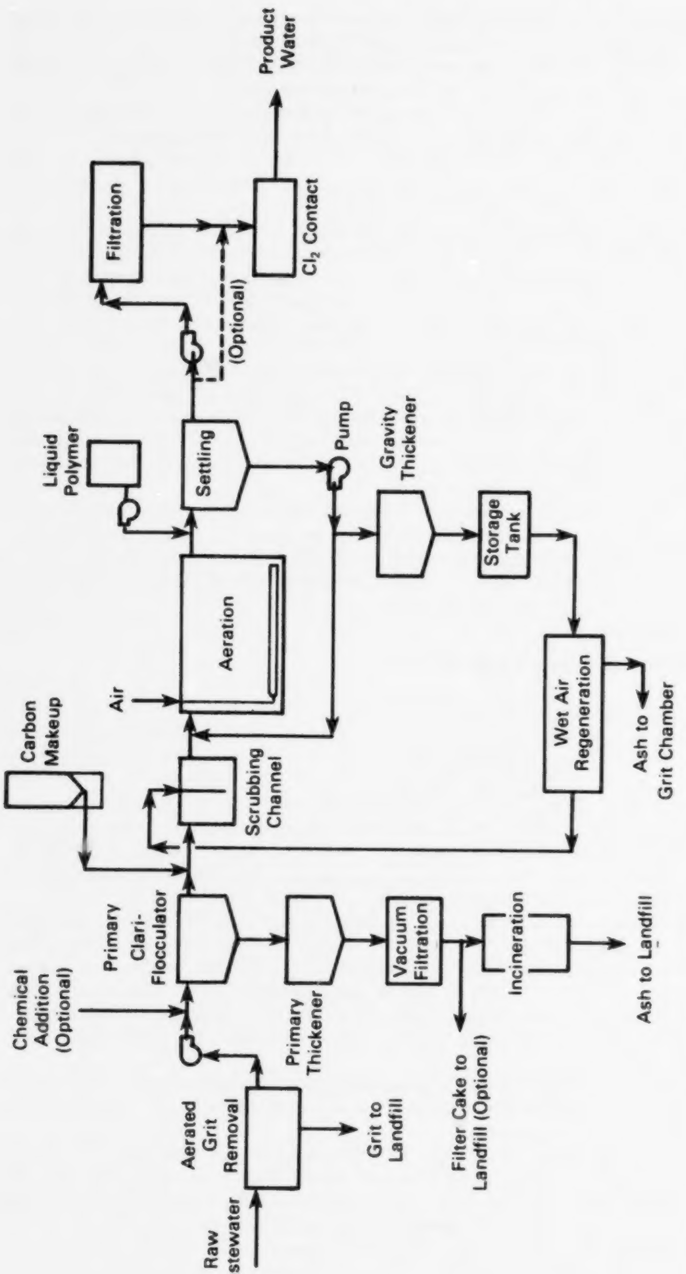
Raw Wastewater
Aerated Grit Removal
Grit to Landfill
Chemical Addition (Optional)
Primary Clari-Flocculator
Primary Thickener
Vacuum Filtration
Filter Cake to Landfill (Optional)
Incineration
Ash to Landfill
Carbon Makeup
Scrubbing Channel
Air
Aeration
Liquid Polymer
Settling
Pump
Gravity Thickener
Storage Tank
Wet Air Regeneration
Ash to Grit Chamber
(Optional)
Filtration
Cl_2 Contact
Product Water

Figure 17. PACT® flow diagram (Courtesy of Zimpro, Inc.).

Thermal reactivation, the method most commonly used for GAC, particularly in municipal waste applications, achieves the greatest degree of restoration of original adsorption properties. In this process the carbon is removed from the adsorber, heated under controlled conditions in a furnace and returned to service. The purpose of reactivation is to restore the original adsorptive capacity of the carbon by removal and/or destruction of adsorbed organic impurities. This is achieved in the thermal process by destructive distillation of adsorbed organic material and steam activation of the char residue. A number of investigations have been carried out on the thermal reactivation of GAC.[108-113]

Thermal reactivation generally involves three consecutive steps; namely:

- drying and volatilization;
- charring; and,
- activating.

The three steps are normally carried out in one furnace having zones of increasing temperature from inlet to outlet. Moisture and volatile adsorbed materials are removed first. Carbon bed temperatures at this stage do not much exceed 100°C because of moisture vaporization. Temperature gradually increases to above 600°C in the subsequent zone, and adsorbed volatile material is driven off by destructive distillation. Only organic char and ash residues remain in the carbon pores at this time. The char is activated in the final zone of the furnace at about 900°C with the addition of steam. Inherently, part of the original carbon is burned along with the char residue; the extent of this "burn off" relates largely to the degree of reactivation required to restore the carbon's adsorptive properties.

There are a number of equipment alternatives for use in reactivating carbon. These include the multiple-hearth furnace, the rotary kiln (either direct or indirect fired), the fluidized-bed furnace, and the electric-belt furnace. Schematic diagrams of these several furnace configurations are given in Fig. 18 (a thru d).

The multiple-hearth furnace--the most widely used alternative to date--consists of a number of fixed stages, or hearths, and a rotating center shaft mounted with rabble arms which move the carbon through each stage. Heating arrangements are usually designed to provide a gas temperature gradient from about 200°C at the inlet or top to 900°C in the lowest hearth.

Fig. 18a illustrates a 6-hearth furnace suitable to reactivate carbon at a municipal IPCT plant. As for any furnace operation, gaseous and particulate emissions must be taken into account; this unit is commonly equipped with an afterburner and a scrubber. The rabble arms are constructed so that the carbon bed is furrowed and turned over as it moves across each hearth. This increases the surface of the bed exposed to the furnace atmosphere, and insures that all of the carbon is effectively reactivated.

The second most common alternative system for carbon reactivation is the rotary kiln. In this furnace configuration (Fig. 18b) carbon moves continuously from one end of the inclined tube to the other under the combined influence of the rotational movement of the tube and of gravity. Gas flow may be either countercurrent or concurrent to the carbon flow. A lower input of steam is needed for concurrent flow operation because water evaporated from the carbon is maintained through the activating zone; emissions are also reduced. The carbon is exposed to the furnace atmosphere through gentle tumbling action as the furnace itself turns. The rotary tube furnace has been used successfully for both activation and reactivation of GAC.

Fluidized bed and electric belt furnaces (Figs. 18c,d) are new to the field of carbon reactivation and are currently undergoing development and evaluation.[112,113]

Reactivation of PAC cannot be accomplished economically in conventional furnaces without extensive modification of both equipment and operating procedures.[102,114] More success has been achieved employing wet oxidation processes to regenerate PAC. In this process, illustrated in Fig. 19, an aqueous slurry of PAC is contacted with an oxygen-containing gas at temperatures of 100°C to 300°C and

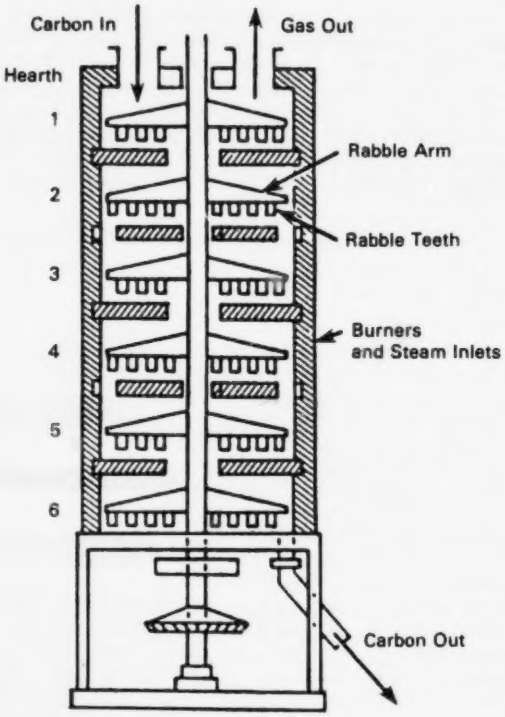
Carbon In
Gas Out
Hearth
1
2
3
4
5
6
Rabble Arm
Rabble Teeth
Burners
and Steam Inlets
Carbon Out

Figure 18a. Schematic diagram of a multiple-hearth regeneration furnace (Courtesy of ICI Americas, Inc.).

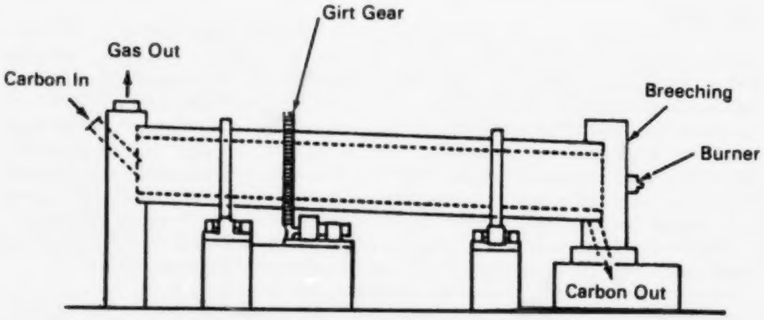
Girt Gear
Gas Out
Carbon In
Breeching
Burner
Carbon Out

Figure 18b. Schematic diagram of a rotary tube regeneration furnace (Courtesy of ICI Americas, Inc.).

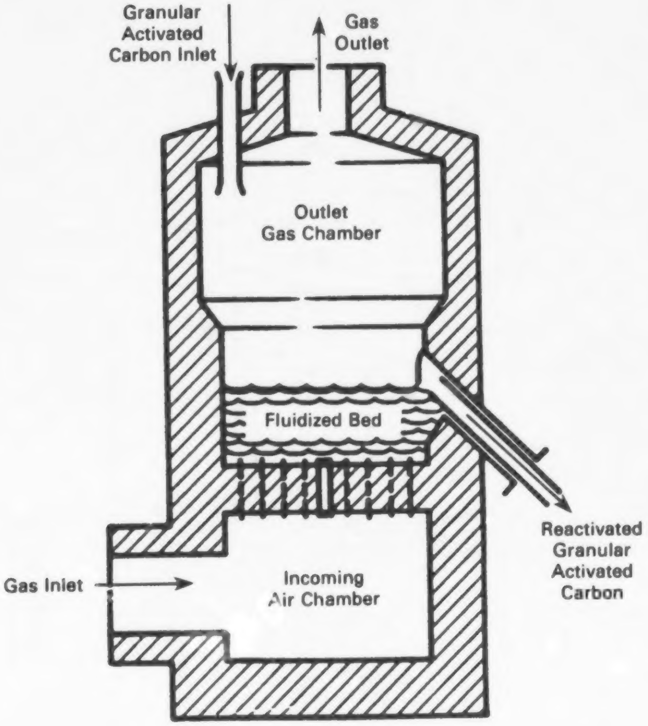
Granular
Activated
Carbon Inlet
Gas
Outlet
Outlet
Gas Chamber
Fluidized Bed
Reactivated
Granular
Activated
Carbon
Gas Inlet
Incoming
Air Chamber

Figure 18c. Schematic diagram of a fluidized-bed regeneration furnace (Courtesy of ICI Americas Inc.).

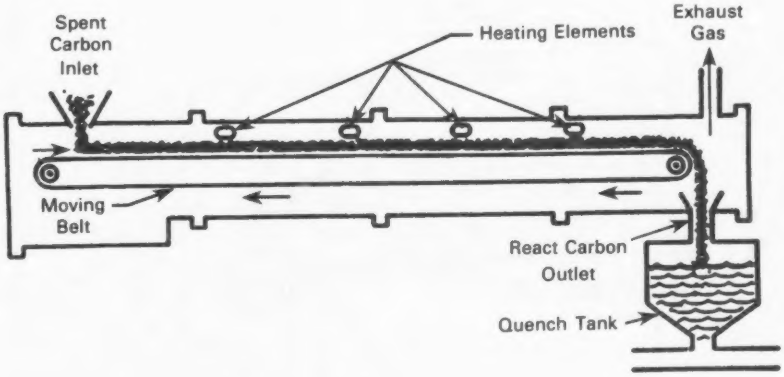
Spent
Carbon
Inlet
Heating Elements
Exhaust
Gas
Moving
Belt
React Carbon
Outlet
Quench Tank

Figure 18d. Schematic diagram of an electric-belt regeneration furnace (Courtesy of ICI Americas Inc.).

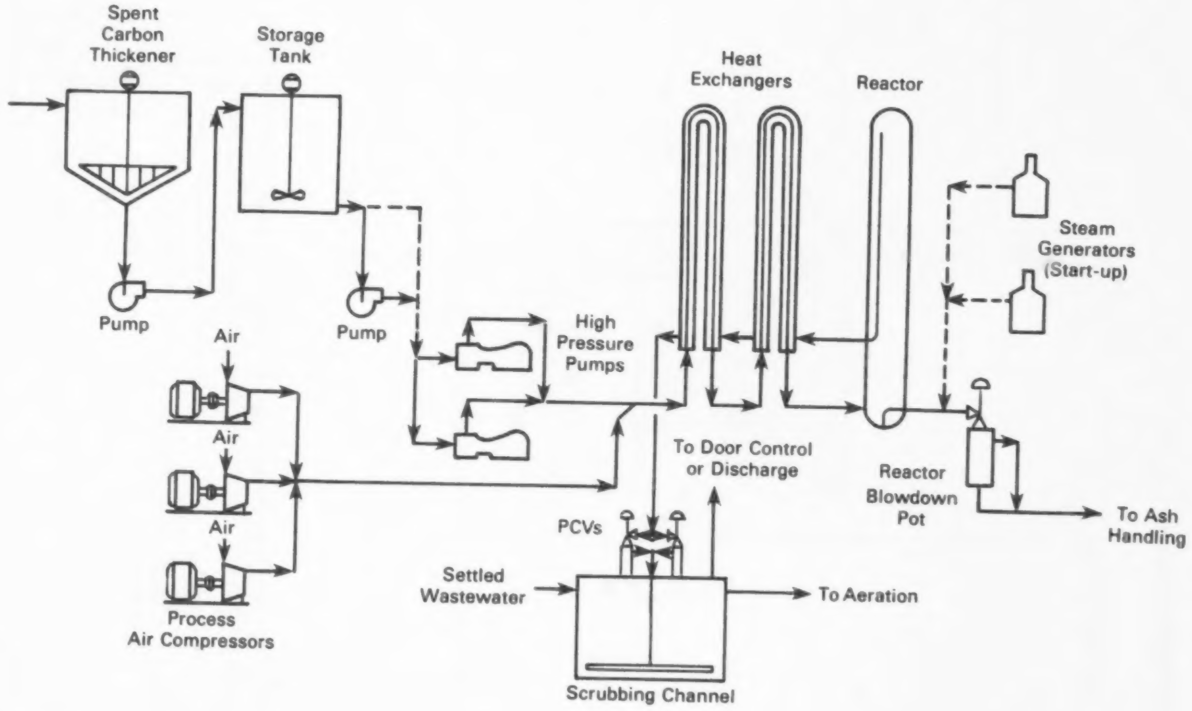
Spent
Carbon
Thickener
Storage
Tank
Heat
Exchangers
Reactor
Steam
Generators
(Start-up)
Pump
Air
Pump
High
Pressure
Pumps
Air
To Door Control
or Discharge
Reactor
Blowdown
Pot
Air
PCVs
To Ash
Handling
Settled
Wastewater
To Aeration
Process
Air Compressors
Scrubbing Channel

Figure 19. Schematic diagram of a wet air regeneration system (Courtesy of Zimpro, Inc.).

pressures of 100 psig to 3000 psig. Actual operating conditions are dependent on the individual application but excellent recovery of carbon properties has been reported.[103,104,115,116]

Carbon loss is an important factor in the operation and operating costs of an activated carbon system. Losses can occur in a number of ways throughout the overall adsorption-reactivation system. Carbon can be oxidized and burned if excess oxygen is allowed to enter the furnace atmosphere. Small particles of carbon can be entrained in the relativley high velocity gas stream moving through the furnace. Attrition losses can occur in all stages of intrasystem transfer and handling. A major cause of carbon losses in many plants is inadvertent overflow and spillage from the system. Entrainment and carry-over in liquid streams can take place wherever excessively high localized velocities exist. This may occur during adsorber backwash or during one of the transport steps in the reactivation system. Finally, apparent losses in volume may relate to changes in the carbon packing characteristics as the particles change shape during handling.

One of the most important aspects of carbon reactivation is the percent adsorption efficiency change incurred during successive reactivations. It is important that the design of any activated carbon facility employing reactivation or regeneration be based primarily on the long-term performance characteristics of the carbon rather than those of the virgin material.

Most operating data from both pilot and full scale installations in which the carbon has been subjected to multiple adsorption-reactivation cycles show similar results. After an initial decrease in adsorption characteristics, carbon performance is generally found to stabilize at a quasi-steady-state level which, with good operational control, can be maintained over a relatively long period.

As noted earlier in this chapter, resistance of the GAC to attrition during use is important. One measure of attrition or particle breakdown is given by changes in mean particle diameter. Data from different applications and installations indicate that such changes are primarily a function of the handling system design and extent of adherence to proper handling procedures.

CASE HISTORIES

It is interesting to note that of the 32 municipal PCT plants currently identifiable in the United States,[117] 21 were identified in the 1973 EPA Carbon Design Manual.[56] This points up the fact that most of these plants were designed and constructed in parallel, eliminating the valuable engineering aid of operating history available to more conventional designs. While many of the plants listed have experienced serious start-up and/or operating difficulties, it must be pointed out that failures and problems have been a function of mechanical design and not process performance. When major failures of seemingly straightforward systems such as sewers still occur as a result of the well delineated process of sulfide corrosion,[118] it is hardly surprising that mechanical problems are experienced in complex physicochemical treatment systems. Indeed, in this light, it is a major accomplishment that advanced municipal wastewater treatment systems have progressed in the single decade of the 1970's from conception through pilot testing, design, construction and operation to demonstrate that high quality water can be produced for discharge or even reuse.

An exhaustive review of all existing PCT plants in the United States--let alone throughout the world--is beyond the scope and intent of this chapter. A reasonable perspective can be provided, however, by briefly examining several plants representing somewhat different design concepts and operational modes. To this end, five specific PCT facilities in the United States are examined with respect to design, performance, and current status. Table 3 summarizes the salient features of the five PCT plants chosen.

Table 3. Comparison of Representative PCT Applications

Site	Treatment	Discharge Point	Capacity (Avg MGD)	Adsorber Type
South Lake Tahoe, CA	AWT	Indian Creek Recreational Lake	7.5	GAC, upflow, packed
Orange County, CA	AWT/RO	Groundwater recharge	15	GAC, downflow, packed
Niagara Falls, NY	IPCT	Niagara River	48	GAC, downflow, packed
Vallejo, CA	IPCT	Carquinez Strait	13	GAC, upflow, expanded
Vernon, CT	PACT	Hockanum River	6	PAC, suspended (PACT®)

South Tahoe, CA

The South Tahoe AWT system was constructed in an effort to protect the exceptional quality of the waters and associated ecosystem of Lake Tahoe in the face of an expanding population and increased use of the lake and surrounding land. The Tahoe water reclamation facility, put into operation in 1965, was the first full-scale municipal plant in the United States to use GAC with on-site reactivation for organic pollutant removal. The plant remains in operation today, and is unique in the field for its long operating record and excellent performance. Over the past 15 years the plant has treated approximately 15 billion gallons of wastewater.

A unique feature of this system is that the high quality water produced by the treatment plant is "exported" from the Tahoe basin and subsequently captured in Alpine County to form Indian Creek Reservoir, a one billion gallon man-made recreational lake.

Design, operating parameters, and a summary of performance are given in Table 4. A plant schematic is presented in Fig. 20.

Orange County, CA

The Orange County wastewater treatment plant is an AWT facility designated Water Factory 21 (WF-21). The name derives from the concept of this facility as a prototype source of supplemental water during the 21st century. The treatment processes employed at WF-21 are designed to produce water suitable for recharge to an underground fresh water aquifer to prevent seawater intrusion. While this particular application is unique to coastal areas, the quality of the water provided by this facility has far-reaching implications for renovation of wastewater for reuse.

The WF-21 facility is designed to treat 15 MGD and, because it discharges the treated water into an aquifer used for potable water supply, the product must meet drinking water quality standards. As a result the facility includes reverse osmosis (RO) as a treatment step subsequent to the conventional AWT treatment steps. Approximately one-third of the AWT effluent is treated with RO prior to reblending for injection.

The GAC treatment facility at WF-21 went on-stream in January 1976, with groundwater injection beginning in October 1976. The addition of RO treatment was made in March 1978 and the system has operated successfully since that time.

Table 5 summarizes design, operating parameters, and the performance of WF-21. Fig. 21 presents a plant schematic.

Niagara Falls, NY

With a capacity of 48 MGD, the IPCT treatment facility at Niagara Falls represents the largest such system yet designed. The IPCT system was chosen because of the concomitant requirements of secondary quality effluent and treatment of significant quantities of industrial wastes. System design was completed in 1972, and therefore relied heavily on pilot data accumulated at Niagara Falls and other sites. The facility was partially completed in 1977 and began to treat wastewater in April of that year. The full IPCT system, including the GAC adsorbers, went on-stream in January 1978, but has operated on only an infrequent basis due to mechanical problems.

The design of Niagara Falls plant includes direct application of coagulated, settled wastewater to the GAC adsorbers. This concept utilizes the GAC as a medium for both filtration and adsorption, and represents an economic advantage by eliminating separate filters. Operation of this facility will generate performance and cost data necessary for evaluation of one of the most innovative and promising treatment methods developed in the recent history of municipal waste treatment.

Table 4. Design, Operating Parameters, and Performance Summary (South Tahoe, CA, Type AWT)

PLANT DESIGN	
DESIGN FLOW (MGD)	7.5
CONTACTOR TYPE	closed, steel
MODE OF OPERATION	upflow, packed bed, parallel
CONTACT TIME (EBCT)	17 min.
HYDRAULIC LOADING (gpm/ft²)	6.5
CARBON DEPTH (ft)	14.5
CARBON TYPE	8×30, GAC
REACTIVATION	multiple hearth (6)
PLANT PERFORMANCE	
BOD	1-3 mg/L
COD	10 mg/L
SS	< 1 mg/L
TURBIDITY	0.2 J.T.U.
PO_4	0.8 mg/L
COLOR	5-6 units
MBAS	0.1 mg/L

A schematic diagram of the Niagara Falls plant is given in Fig. 22. Table 6 is a summary of salient design, operation, and performance characteristics.

Vallejo, CA

The Vallejo facility is an IPCT system which employs filtration ahead of upflow, expanded-bed GAC adsorbers. This design incorporates several new concepts developed during the 1970's specifically for municipal wastewater treatment applications of GAC. The facility was designed early in the decade. Construction proceeded through the mid-1970's and plant start-up occurred during 1978. While limited data are available and system modifications have taken place, it appears that the facility can meet the original design criteria.

Design and operating parameters as well as a summary of performance are given in Table 7. A plant schematic is shown in Fig. 23.

Vernon, CT

Vernon, CT is the first municipality to operate a powdered activated carbon system which includes carbon regeneration. The Vernon facility utilizes the PACT ® concept of combined PAC and activated sludge treatment with wet oxidation for simultaneous destruction of excess sludge and regeneration of the PAC. With an early 1979 start-up and no other full-scale operating data available, this facility, like the IPCT systems at Niagara Falls and Vallejo, characterizes the innovation and development encouraged and supported by the EPA during the 1970's. The attempt

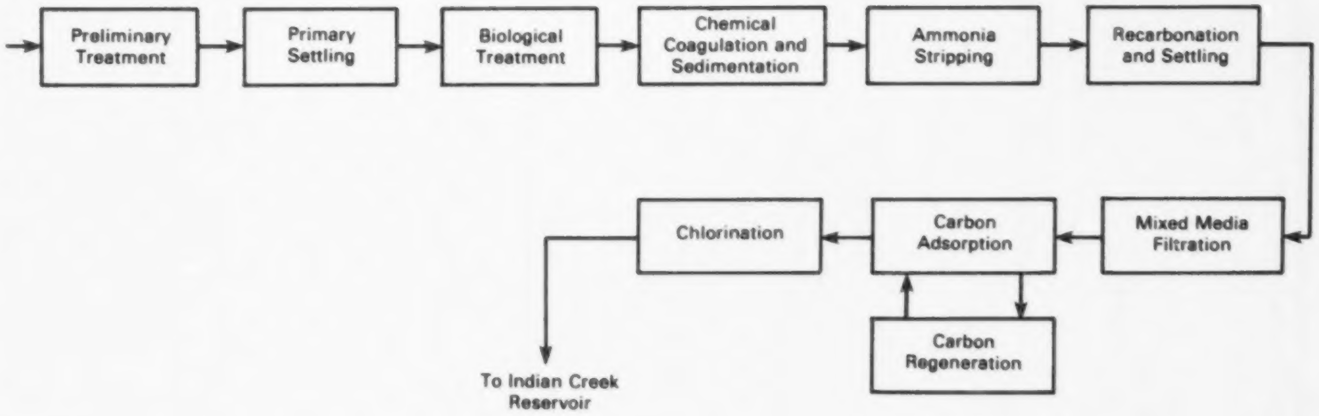
Preliminary Treatment
Primary Settling
Biological Treatment
Chemical Coagulation and Sedimentation
Ammonia Stripping
Recarbonation and Settling
Mixed Media Filtration
Carbon Adsorption
Carbon Regeneration
Chlorination
To Indian Creek Reservoir

Figure 20. Tertiary treatment schematic South Lake Tahoe, CA (from Reference 56).

Table 5. Design, Operating Parameters, and Performance Summary (Orange County, CA, Type AWT/RO)

PLANT DESIGN

DESIGN FLOW (MGD) 15
CONTACTOR TYPE closed, steel
MODE OF OPERATION downflow, parallel
CONTACT TIME (EBCT) 30 min.
HYDRAULIC LOADING (gpm/ft²) 2.3
CARBON DEPTH (ft) 28
CARBON TYPE 8×30 GAC
REACTIVATION multiple hearth (6)

PLANT PERFORMANCE	GAC	RO
BOD	–	–
COD	15 mg/L	1.5 mg/L
SS	<1 mg/L	<1 mg/L
TURBIDITY	<1 J.T.U.	<1 J.T.U.
PO_4	1.3 mg/L	<1 mg/L
COLOR	–	–
MBAS	–	–

to combine the ability of activated carbon to adsorb recalcitrant organic materials with the proven economic advantages of activated sludge treatment may well result in a blend of the best of both processes.

The potentials for high quality performance and economic benefits of regenerating the powdered carbon combine to identify the Vernon facility as one to monitor closely, for this may represent a trend for future municipal wastewater treatment.

The design, operating parameters, and performance of the Vernon plant are presented in Table 8. Fig. 24 provides a schematic diagram of this facility.

THE FUTURE OF PCT IN MUNICIPAL WASTE TREATMENT

Research and development needs relative to the application of PCT processes--specifically GAC and PAC processes--in municipal waste treatment are much akin to those in water and industrial waste treatment applications. DiGiano[58] and O'Brien, et al.[57] have provided complementary discussions of these needs, and little more need be said here in this regard. A larger question, however, is what the future holds for PCT applications in municipal waste treatment.

The economic climate of the United States, indeed the world, during the closing years of the 1970's forced a re-evaluation of the concept that clean water is worth any price. Rigorous redeterminations of cost-effectiveness and cost-benefit relationships have notably slowed the progress of PCT in the municipal waste treatment field. Future considerations of PCT processes for removal of conventional pollutants will

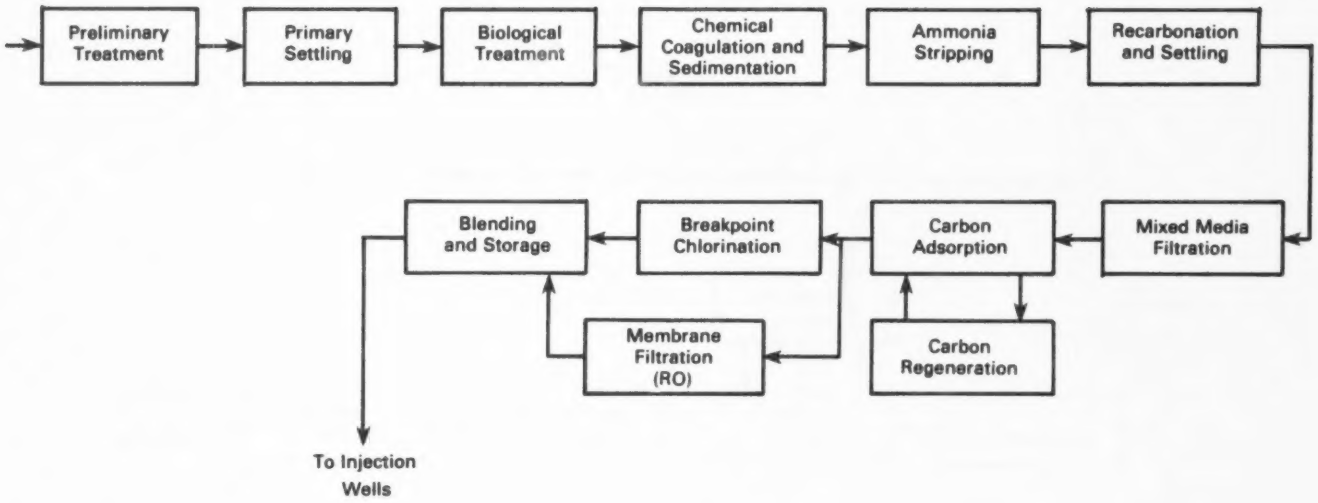
Preliminary Treatment
Primary Settling
Biological Treatment
Chemical Coagulation and Sedimentation
Ammonia Stripping
Recarbonation and Settling
Mixed Media Filtration
Carbon Adsorption
Carbon Regeneration
Breakpoint Chlorination
Membrane Filtration (RO)
Blending and Storage
To Injection Wells

Figure 21. Tertiary treatment schematic Orange County, CA (from Reference 56).

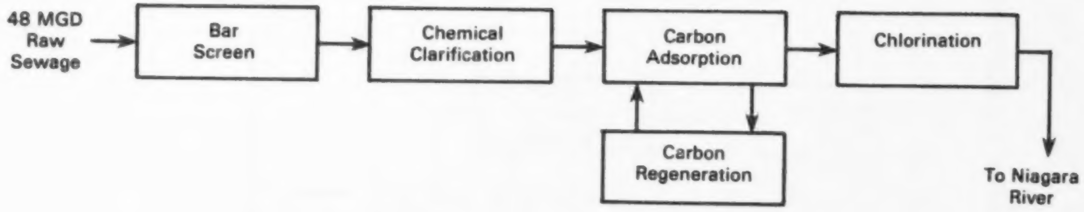
48 MGD
Raw
Sewage
Bar
Screen
Chemical
Clarification
Carbon
Adsorption
Carbon
Regeneration
Chlorination
To Niagara
River

Figure 22. Physical chemical treatment schematic Niagara Falls, NY (from Reference 56).

Table 6. Design, Operating Parameters, and Performance Summary (Niagara Falls, NY, Type IPCT)

PLANT DESIGN	
DESIGN FLOW (MGD)	48
CONTACTOR TYPE	open, concrete
MODE OF OPERATION	downflow, parallel
CONTACT TIME (EBCT)	40 min.
HYDRAULIC LOADING (gpm/ft^2)	1.7
CARBON DEPTH (ft)	8.75
CARBON TYPE	8×30 GAC
REACTIVATION	multiple hearth (6)
PLANT PERFORMANCE	
BOD	
COD	75% removal
SS	90% removal
TURBIDITY	
PO_4	
COLOR	
MBAS	

Table 7. Design, Operating Parameters, and Performance Summary (Vallejo, CA, Type IPCT)

PLANT DESIGN	
DESIGN FLOW (MGD)	13
CONTACTOR TYPE	open, concrete
MODE OF OPERATION	upflow, expanded bed, parallel
CONTACT TIME (EBCT)	25 min.
HYDRAULIC LOADING (gpm/ft^2)	6
CARBON DEPTH (ft)	16
CARBON TYPE	12×40 GAC
REACTIVATION	multiple hearth (6)
PLANT PERFORMANCE	
BOD	25 mg/L
COD	45 mg/L
SS	7 mg/L
TURBIDITY	
PO_4	
COLOR	
MBAS	

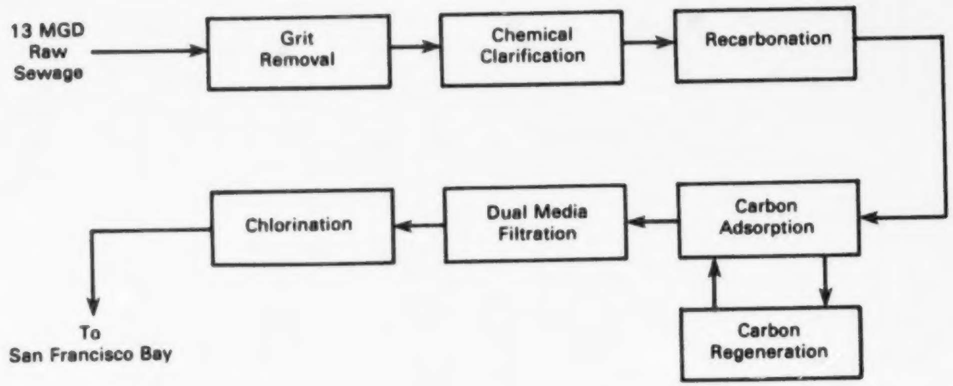
13 MGD
Raw
Sewage
Grit
Removal
Chemical
Clarification
Recarbonation
Carbon
Adsorption
Carbon
Regeneration
Dual Media
Filtration
Chlorination
To
San Francisco Bay

Figure 23. Physical chemical treatment schematic Vallejo, CA (after Reference 56).

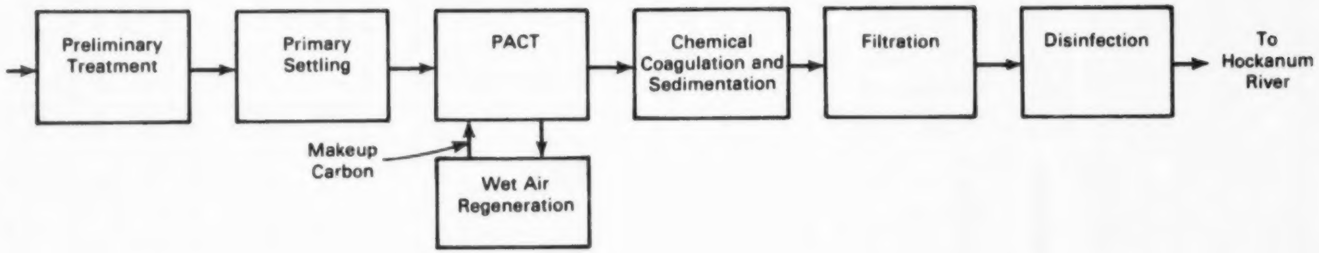
Preliminary Treatment
Primary Settling
PACT
Makeup Carbon
Wet Air Regeneration
Chemical Coagulation and Sedimentation
Filtration
Disinfection
To Hockanum River

Figure 24. PACT® treatment schematic Vernon, CT.

Table 8. Design, Operating Parameters, and Performance Summary (Vernon, CT, Type PACT®)

PLANT DESIGN	
DESIGN FLOW (MGD)	6
CONTACTOR TYPE	suspended - aeration
MODE OF OPERATION	PACT
CONTACT TIME (EBCT)	-
HYDRAULIC LOADING (gpm/ft^2)	X
CARBON DEPTH (ft)	X
CARBON TYPE	PAC
REACTIVATION	Wet Oxidation
PLANT PERFORMANCE	
BOD	<20 mg/L
COD	-
SS	<10 mg/L
TURBIDITY	-
PO_4	-
COLOR	<5 APHA units
MBAS	-

depend on the specific needs of critical geographic regions, and on performance and economic data yet to be obtained from currently operating systems.

Conversely, concern with respect to the control of toxic and hazardous waste materials is expanding markedly, and it is in this area that PCT processes, and particularly activated carbon, are most generally applicable. Legislation has taken specific issue with discharge of toxic and hazardous substances from publicly-owned treatment works (POTWs). Moreover, it has given the municipal governments responsible for operation of POTWs the authority to identify and control all discharges of such substances to tributary sewer systems. Based on these developments, the future of PCT processes in municipal waste control--either as treatment operations under the direct control of municipalities or as pretreatments required of dischargers to the collecting sewers of POTWs--seems predestined.

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THE IMPACT OF ORGANIC SUBSTANCES ON MUNICIPAL WASTEWATER REUSE

J. Carrell Morris, PhD and John F. Donovan

INTRODUCTION

Rationale for Reuse

With few exceptions, the development of municipal wastewater-reuse facilities and current research in this field have focused on reuse for nonpotable purposes. Nonpotable reuse can be defined as the substitution of "reclaimed water" for waters of potable quality that are now being used for nonpotable purposes. The U.S. Environmental Protection Agency (EPA) encourages reuse by defining it as an "innovative/alternative technology" that may be eligible for additional funding under the Clean Water Act of 1977. The benefits in this type of water reuse are several[1]:

- The demand on limited, high-quality sources of water is relieved, so that such sources can serve larger populations or so that the useful life of these sources can be extended.
- The cost and energy requirements of providing reclaimed water may be less in some instances than the cost of developing additional high-quality freshwater sources, even when these are availabe.
- Discharge of pollutants to watercourses is reduced.
- Other priorities--such as the preservation of open spaces, of recreational areas or of agricultural lands--may be realized, because a supply of water necessary for each development may be made available that otherwise could not be dedicated to these uses.
- The risks to the population from the life-long ingestion of the harmful organic contaminants in polluted waters are virtually eliminated, since high-quality waters are reserved for potable use.

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Mr. John F. Donovan is a project engineer in the Environmental Engineering Division of Camp, Dresser and McKee, Inc., which he joined on receiving his Bachelor of Science and Master of Science degrees in civil engineering at Northeastern University. He has participated in several major projects involving design evaluation of wastewater collection and treatment facilities, studies of sludge management and effluent disposal, and research on innovative methods of sludge stabilization and water reuse. He served as overall project manager for "Guidelines for Water Reuse" which was published as an EPA manual. Mr. Donovan is the author of several technical papers on water reuse.

The last point is particularly important in the context of this monograph: wastewater reuse is one way to avoid the use of polluted sources for potable supplies. Two other broad options are available for producing potable waters from polluted sources: (1) eliminating the pollutants at their source--source control--or (2) monitoring and removing the pollutants by treatment. Both of these approaches can be difficult where sources drain urban and industrial areas.

The difficulty in source control is exacerbated by the continual development of new chemicals. Some 1,000 new chemicals are introduced by industry annually. The U.S. General Accounting Office (GAO), reviewing the status of the control of chemical exposures in industry, has concluded that. . ."It will take more than a century to establish needed standards for substances already identified as hazardous. . .The problem is compounded because new substances, which may warrant standards, are being introduced faster than standards are being established on existing substances"[2]. If this is the case for chemicals in the industrial setting, the situation is far more critical in the environment.

Monitoring and removing organic substances by treatment is also difficult. Treatment may be accomplished at a wastewater-treatment facility discharging to a waterway that serves as a source of potable supply, or at a water-treatment facility drawing from a polluted source, or both. Routine monitoring and treatment for removal for a wide variety of organic chemicals is not currently practiced because the technology is complex and projected costs appear too high for the thousands of relatively small municipal and private authorities responsible for wastewater disposal and water supply.

Impact of Organic Substances on Reuse

Organic substances present in reclaimed water have not been considered an important factor in most reuse planning. Where reuse is projected for nonpotable purposes only, the presence of potentially harmful organic chemicals in the reclaimed water has not been found generally, to be of great consequence.

Such is not the case, of course, where reuse for potable purposes is contemplated. In such instances, the full range of concerns explored in the water supply section of this monograph must be considered. Reclaimed water generated from domestic wastewaters and treated to sufficient levels may be of better quality than water taken from sources subject to heavy contamination from synthetic organic substances.

Such reuse applications as urban landscape and agricultural irrigation, industrial processing (other than food processing), cooling, toilet flushing, most commercial applications (e.g., car washing), and recreation generally are not affected by the presence of organic material of the types and concentrations normally encountered in municipal secondary effluents. Only where irrigation is used on crops that are to be used for animal feed, or directly for human feed need there be a concern for human health. Up to now, most attention in such situations has been given to concentrations of heavy metals, but as the number of reuse projects continues to grow, more attention needs to be given to the possible accumulation of organic substances in crops and the significance of these substances both to the growth of the crops themselves and to the health of animals and humans who use these crops for food.

The following sections deal with types and examples of municipal reuse, the need for control of organic substances in waters intended for reuse, quality requirements for organic substances, methods of control of organic substances, an assessment of present problems, and future outlook.

TYPES AND EXAMPLES OF MUNICIPAL REUSE

Reuse can be classified broadly as direct and indirect. Direct reuse is the planned and engineered use of treated wastewater for some beneficial purpose such as irrigation, recreation, industry, or groundwater recharge. Indirect reuse of wastewater occurs when wastewater already used for domestic or industrial purposes is discharged into fresh surface or groundwaters and withdrawn downstream in diluted form. An example of indirect reuse is the Upper Occoquan AWT Plant in Virginia. There, highly treated effluent is discharged to a stream tributary to the Occoquan Reservoir, a potable water source for a large portion of Fairfax County, Virginia. This text deals solely with direct, engineered "pipe-to-pipe" use of municipal wastewater.

Fig. 1 and Table 1 illustrate the number and variety of nonpotable reuse applications already used in pilot- or full-scale installations throughout the United States. Potable reuse has not been pursued as strongly as nonpotable reuse, because of health concerns; however, potable reuse is being evaluated on a pilot-scale basis in Denver, Colorado. The figures used in Table 1 are taken from two nationwide surveys [3,4] completed in 1971 and 1979, respectively.

The 1979 survey reported reuse projects underway in about 25 states.

The California Department of Health Services in 1977-78 found reuse underway at 363 locations in that state.[5] As in the nationwide surveys, the great majority of projects--88 percent--involved types of agricultural or landscape irrigation. Most of the individual irrigation users reportedly utilize only relatively small volumes of reclaimed water. Another similarity among the California and nationwide surveys is the finding that relatively large volumes of reclaimed water are being used in industry and for groundwater-recharge purposes.

The State of California, where the majority of all U.S. reuse is taking place, offers several good examples of various types of reuse projects. At the Irvine Ranch Water District, a coagulated, filtered, and disinfected secondary effluent is fed through a 50-mile reclaimed-water distribution network for use in landscape and agricultural irrigation. Eventually, the district will be reclaiming and distributing up to 15 mgd for nonpotable uses, including expanded agricultural irrigation and possible industrial use.

Drawing wastewater directly from an interceptor has worked successfully since 1962 at Whittier Narrows in a reuse program administered by the Los Angeles County Sanitation District (LACSD). Wastewater diverted from a major regional interceptor is given conventional activated-sludge secondary treatment, filtration, and chlorination at the Whittier Narrows Water Reclamation Plant. The reclaimed water (along with reclaimed water from the San Jose and Pomona plants also administered by LACSD) is then applied to spreading areas for recharge of two large groundwater basins a few miles east of Los Angeles. The operation has several major attributes:

- The reclamation plant receives mostly domestic wastes. It is upstream of major industrial discharges that might make the plant's effluent unsuitable for recharge purposes.
- Sludge from the reclamation plant is diverted back to the sewer for eventual treatment downstream, serving to reduce system complexity and cost at the upstream reclamation plant, and also to improve site landscaping possibilities, which enhances public acceptance.
- There are savings in capacity--and total costs--for conveyance and treatment facilities downstream.
- Because the plant draws a constant flow from the interceptor, its treatment performance is improved.
- In the event of a treatment-plant upset, the unsuitable effluent can be diverted back to the sewer for treatment downstream.

This system proved so successful that LACSD has since constructed four additional reclamation facilities (Pomona, Los Coyotes, Long Beach and San Jose Creek).

A major EPA-funded wastewater reclamation facility is the Orange County, California, Water District's Water Factory 21. This 15-mgd facility is designed to treat unchlorinated secondary effluent from a nearby municipal wastewater treat-

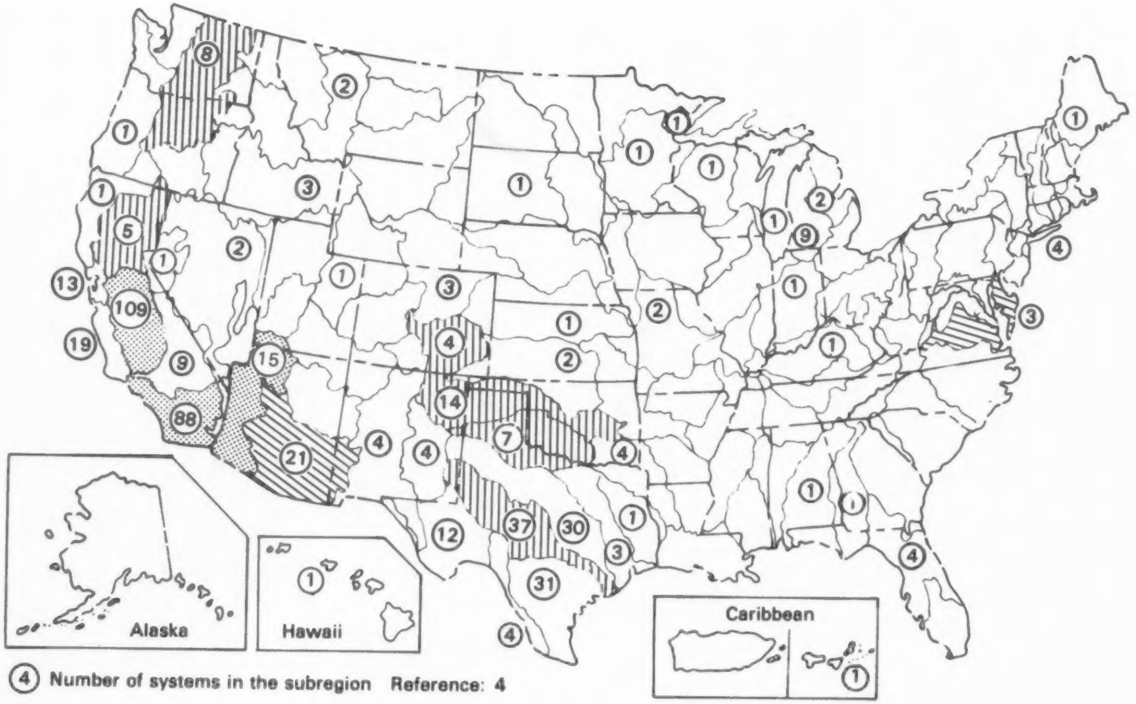

Alaska
Hawaii
Caribbean
④ Number of systems in the subregion   Reference: 4

Figure 1. Distribution of existing water reuse projects in the United States.

Table 1. Reuse Projects in the United States

Type of Reuse	Number of Projects 1971	1979
Agricultural/landscape irrigation	400	470
Industry	15	29
Groundwater recharge	10	11
Fish propagation, recreation and other	5	26
Totals	430	536

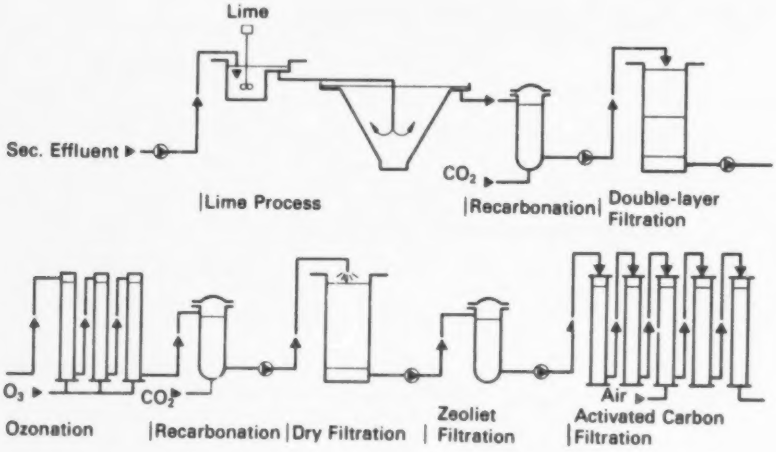
ment facility. The unit processes include lime clarification with sludge recalcining, air stripping, recarbonation, prechlorination, mixed-media filtration, granular activated carbon adsorption with carbon regeneration, final chlorination and reverse osmosis demineralization. The effluent is blended with potable water and injected into the groundwater to protect potable groundwater aquifers from salt-water intrusion.

The State of California Department of Health Services has set restrictions on reuse programs that involve recharge of groundwater aquifers.[6] Recent research results indicate that viruses and organic contaminants show measurable rates of migration in aquifer recharge systems. An amendment to the agency's regulations calls for a strict, case-by-case review of projects based on factors such as "level of treatment provided; effluent quality and quantity; spreading area operations; soil characteristics; hydrogeology; residence time; and distance to withdrawal."

In Contra Costa County, California, the Central Contra Costa Sanitary District is responsible for much of the wastewater treatment and disposal function in the county's industrial areas. Most of the major oil and chemical companies in the area purchase water from the Contra Costa Water District. In 1972, the Sanitary and Water Districts signed a contract providing for sale of the Sanitary District's effluent to the Water District for further treatment and resale to several industrial users. The Sanitary District provides secondary treatment and filtration of 15 to 30 mgd, with delivery to a clearwell operated by the Water District. The Water District operates an ion-exchange softening facility and a storage and distribution system to supply industries with 15 mgd for cooling-tower usage. The project is designed to meet an ultimate 30-mgd demand for various industrial uses, but mostly for cooling. In the development of the Contra Costa County project, consideration was given to the prospect that various organic substances might contribute to potential cooling-tower corrosion by increasing biological growths. A test program showed that biological growth could be controlled by periodic use of chlorine and other nonoxidative biocides.

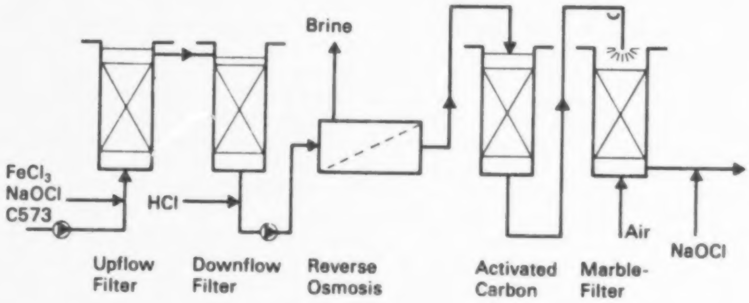
Reuse projects are also in operation in other countries: The Netherlands, Israel, South West Africa and Singapore. At Dordrecht, The Netherlands, pilot testing of potable reuse is underway to evaluate the use of reclaimed water as an alternative to the highly contaminated Rhine and Meuse Rivers as sources of supply.[7] Schematics of the physical-chemical lime process train and the reverse-osmosis process train are shown in Fig. 2. The lime-process employed was found not to be effective in removing organic compounds. No removal of volatile halogenated organic substances or non-polar organic chlorine was noted. However, many organic compounds in the activated-sludge facility effluent were actually lower than mean concentrations in the drinking water of Dordrecht (see Fig. 3).

Reverse-osmosis test results at Dordrecht are shown in Table 2. The groups of halogenated aliphatics, benzene and C_1 and C_2 alkyl benzenes, naphthalene,


Lime
Sec. Effluent
Lime Process
CO_2
Recarbonation
Double-layer Filtration
O_3
CO_2
Ozonation
Recarbonation
Dry Filtration
Zeoliet Filtration
Air
Activated Carbon Filtration

Reference: 7

a. Physical-Chemical System


Brine
$FeCl_3$
NaOCl
C573
HCl
Air
NaOCl
Upflow Filter
Downflow Filter
Reverse Osmosis
Activated Carbon
Marble-Filter

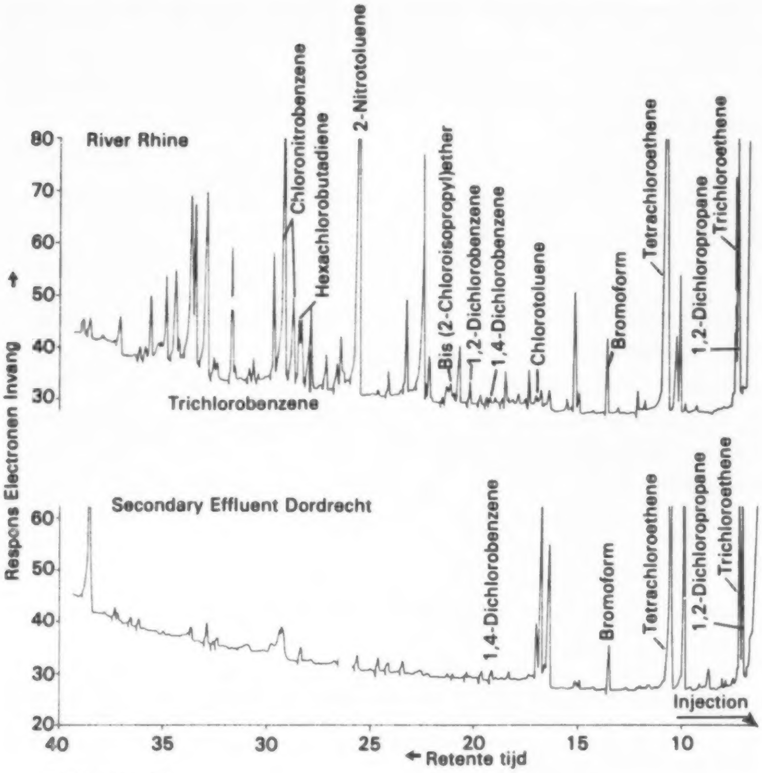
Reference: 7

b. Reverse-Osmosis System

Figure 2. Schematic diagram of pilot testing systems for potable reuse, Dordrecht, The Netherlands.

alkalated naphthalenes, sulfonamides and alkylphenols were not removed effectively by this process. However, effective removal was attained for alkanes, alkylated benzenes with long side chains, indane and alkylated indanes, organic phosphates, chlorophosphates, phthalates and cyclic hydrocarbons. With subsequent activated-carbon filtration, substantial additional removal of nearly all organic substances was achieved.

The largest and most advanced wastewater reclamation scheme in Israel is the Dan Region Project located near Tel Aviv.[8] Planning for this facility began in 1965.



Reference: 7

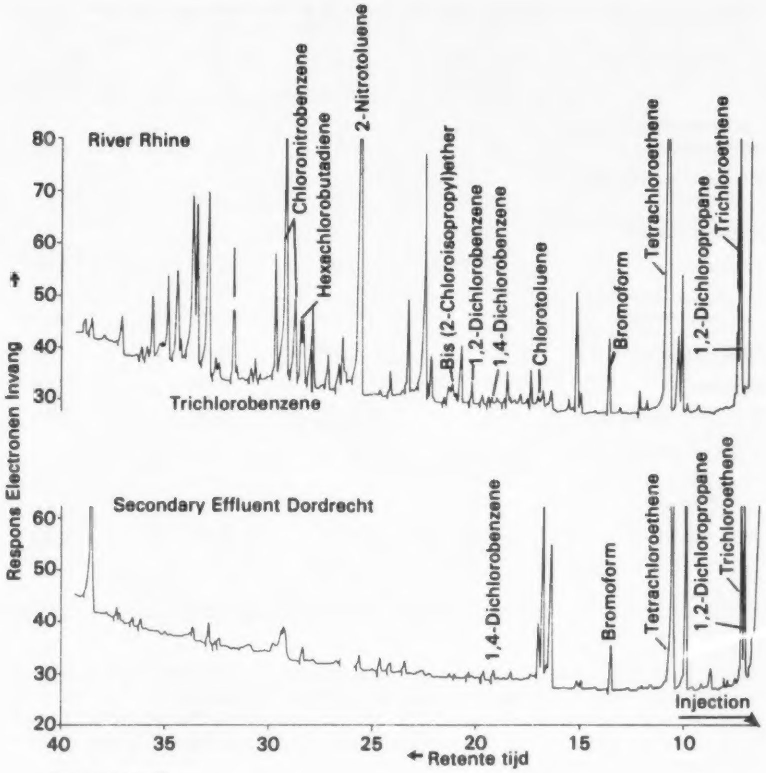
Figure 3. Chromatogram of Rhine River water and secondary effluent - Dordrecht, The Netherlands.

Wastewater undergoes three major treatment processes prior to groundwater recharge by means of spreading basins:

- Biological treatment in oxidation ponds
- High-lime treatment, and
- Detention in polishing ponds.

The recharged water will be extracted from the ground by means of recovery wells and conveyed to the southern part of the country in a separate transport main system. This high-quality water will be available for unrestricted agricultural, industrial and municipal nondomestic uses. An earlier objective, production of a potable product, was dropped in 1975, due primarily to public-health considerations.

The well-known Windhoek reclamation plant in South West Africa is still the only full-scale facility in the world at which wastewater is reclaimed for direct potable reuse. Intermittently since 1968, the 1-mgd facility has provided 10 to 20 percent of the potable-water demand for the City of Windhoek. A Water Research Commission has carried out studies on health effects of using reclaimed water.[9] In one study, 18 known toxic compounds were inoculated into the feed water of a pilot



Reference: 7

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Table 2. Removal of Organic Micropollutants in the Reverse-Osmosis System

Compounds μg/L	Secondary Effluent	Feed R.O.	Effluent R.O.	Effluent Marble Filter
Halogenated aliphatic hydrocarbons	21	8.5	11	1.1
Benzene $+C_1+C_2$ alkylbenzenes	0.3	0.3	0.25	0.1
Sulphonamides	3.3	3.3	3.1	-
Alkylphenols	0.69	0.69	0.31	0.36
Naphthalene + alkylnaphthalenes	0.2	0.1	0.05	0.01
Hydronaphthalenes	0.12	0.19	0.06	-
Alkanes	0.2	0.9	0.05	0.05
C_3-C_8 alkylbenzenes	5.7	3.36	0.76	0.13
Indane + alkylindanes	0.75	0.75	0.05	-
Phosphates + chlorophosphates	0.5	0.5	0.06	-
Phthalates	10.2	1.7	0.23	0.13
Cyclic hydrocarbons	1.13	1.13	0.11	0.2

reclamation plant. The plant reduced the toxicants by more than 99.9 percent, to values from 0 mg/L to 6 mg/L in the final water. In another study, only two polynuclear aromatic hydrocarbons were detected in the plant effluent, while ten were detected in the influent. The two in the effluent (pyrene and fluoranthene) are not of toxicological importance.

In Singapore, reuse of wastewater effluents has been practiced since 1915. Since the mid-1960s, a coagulated, filtered, and disinfected reclaimed water has been used by industry, for irrigation and through a separate distribution network for toilet flushing in high-rise residential apartments.

NEED FOR CONTROL OF ORGANIC SUBSTANCES IN WATERS INTENDED FOR REUSE

Wastewater effluents from standard secondary treatment plants, even from those using intensive or extended biological oxidation, contain a wide variety of organic materials, amounting overall to 20 to 100 mg per liter. Although much of this organic material is proteinaceous, fatty or carbohydrate-like, derived from microbial metabolism, a significant fraction consists of synthetic organic chemicals resistant to aerobic biochemical attack. Such resistance is indicated by the high ratios of chemical to biological oxygen demand found for secondary effluents, often as great as 5 to 1.

Although the proportion of synthetic organic materials may increase with the fraction of industrial wastewater admitted to the municipal sewerage system, the absence of industrial discharges does not mean that synthetic organic structures will be absent. Such substances as polycyclic aromatic hydrocarbons (PAH) pesticides and polychlorinated biphenyls are nearly ubiquitous. In addition, household and small business use of organic cleaning solvents, deodorants like the dichlorobenzenes, cresols and terpenoid materials contributes additional synthetic organic structures to purely domestic-type sewages. Standard treatment is ineffective for removal of many of these substances, so that they remain as components of the treated effluents.

When the effluents are discharged to riverine waters, the organic materials present are subjected to further processes of dilution, biochemical or chemical reactions, volatilization, and adsorption. Nonetheless, many of the added compounds continue to exist in the receiving rivers in currently measurable concentrations over long distances and for extended periods of time. Intensive investigations of large receiving rivers like the Ohio, the Mississippi, and the Rhine have shown that they each contain 500 or more trace organic compounds of which 50 to 100 are of specific concern with regard to toxic or carcinogenic properties.

The situation is more critical when the effluents are to be employed for some sort of direct reuse, such as groundwater recharge and/or potable reuse. Because the factor of dilution is missing or greatly reduced, the opportunity for long-term environmental changes is also diminished. For example, Garrison and Miele pointed out a few years ago: "the constituents of major concern in groundwater-recharge systems are trace organics of unknown health effects"[10]; others have expressed similar concerns with regard to these contaminants in waters intended for similar types of reuse. These health concerns are not as critical, however, in water intended for nonpotable reuse.

Unfortunately, there are few data relating to the magnitude of the problems posed by these trace organic substances. Recently, Roberts, McCarty and coworkers[11] acquired imformation on some California wastewaters, including both standard secondary effluents and those treated by advanced methods. Smith, Englande and coworkers[12] reported trace organic analyses of the effluents of a number of advanced waste treatment installations around the country. These studies show that many identifiable organic compounds of toxicological interest are present in normal sewage effluents and that several of these persist through current advanced waste treatment processes, usually in much reduced concentrations.

McCarty, Reinhard and Argo, in their study of the Orange County Advanced Waste Treatment Plant, Water Factory 21, adopted as tentative maximum contaminant levels (MCLs) for trace organic substances the concentrations of 1 microgram per liter for nonchlorinated substances and 0.5 microgram per liter for chlorinated ones.[13] The procedure is a crude one, but the attempt is worthwhile and the selected values appear reasonable in the absence of specific toxicological and carcinogenic data. Based on their values, the types of substances presenting the greatest problems and the greatest need for controls are the volatile chlorinated hydrocarbons, dichloro-benzenes and phthalate esters.

Researchers caution against overreaction to the presence of trace organic substances in reclaimed wastewater. As Lennette and Spath[14] state, "In struggling with the complexities of establishing goals or standards for treatment of recycled wastewater in order to provide reasonable assurance against health risks, one should be wary of insisting that nothing less is acceptable than the ultimate degree of purity which modern technology can achieve. This technology is immensely costly and should be reserved for those situations in which there is a genuine and demonstrable need. Because modern technology permits measurement of such minute traces, it does not necessarily follow that public health will be better protected or the public interest better served by embracing such sweeping goals as the complete removal of all viruses of human origin from any waters that man may contact or equivalent ideals such as 'zero-levels' and 'no-threshold levels' of toxic or carcinogenic substances."

In some instances, the presence of organic matter in general, as a medium for undesirable biological growths, for the clogging of soils or other finely apertured materials, or for sensory problems, may call for regulation of parameters relating broadly to the organic content, such as BOD, COD, TOC, CCE, color, odor, MBAS and phenols. Necessary limitations on these more traditional engineering parameters can now be met in almost all instances by advanced treatment procedures developed during the past decade. Thus, they do not present as great a need for future research and acquisition of data as the trace organic substances do.

QUALITY REQUIREMENTS FOR ORGANIC SUBSTANCES IN REUSE OF MUNICIPAL WASTEWATERS

General Aspects

With the exception of general parameters relating to organic content such as BOD, COD or TOC, the organic substances that might affect the nonpotable reuse of municipal wastewater had received little attention prior to 1975 and are hardly mentioned in any formalized tabulations of criteria for water reuse. This is partly because suitable techniques for measuring most individual organic substances were not generally available before 1975. Perhaps a more important factor, however, is that the concentrations of organic contaminants, other than those natural materials associated with usual household activities, are generally so small--a few micrograms per liter or less--that deleterious effects in nonpotable reuse have not been considered significant.

Accordingly, it is necessary to discuss organic substances of *potential* concern, based upon what has been learned about the types of compounds present in wastewaters and treated effluents during the past decade, rather than to describe standards and control measures for established hazards. Until the middle of the decade, the only specific organic contaminants to attract much attention in connection with reuse were phenolic compounds and synthetic detergents, the former because of tastes and odors, the latter because of foam-producing properties. Beginning about 1974, however, with the development of gas-chromatographic/mass-spectrometric techniques for the isolation and identification of specific organic compounds from effluents and polluted waters, interest in other classes of organic substances began expanding rapidly. Among the types of compounds receiving particular attention are those, like chlorinated hydrocarbons or nitrosoamines, that appear to present significant health hazards and those, like some chlorinated aromatic compounds or phthalate esters, that exhibit strong resistance to chemical and biological degradation in the environment. Until now, the concern has reached the stage of quantitative expression as criteria or standards only in connection with the reuse of treated wastewater for groundwater recharge. For most other types of reuse, as Russell Culp[15] pointed out in a paper at the Groundwater Recharge Symposium of September, 1979 in Pomona, California, "The trace organics problem is no greater in reclaimed wastewater than it is in natural water supply sources. All indications are that resolution of the trace organics problem in reclaimed water will be simultaneous with resolution of the same problem in drinking water supplies, or sooner."

Dr. Takashi Asano of the California Office of Water Recycling has identified five major categories for municipal water reuse in a descending order of anticipated volume of reuse. These are: land application (irrigation for crops, landscape plantings or natural vegetation); impoundment for recreational facilities; industrial cooling or process water; groundwater recharge; direct consumptive use. Generally speaking, the same order of ranking applies with regard to quality requirements, those for direct potable use being the most stringent, of course. With some exceptions, criteria for specific organic pollutants will rank similarly.

Agricultural and Landscape Use

Historically, quality requirements on reclaimed water for use agriculturally have not been too demanding. Attention has been focused chiefly on saline properties and on biological health hazards. Adequately disinfected standard secondary effluent has been satisfactory for irrigation in many cases. Even primary municipal effluent has on occasion been accepted as suitable for use on forage and grain crops.

A recent Office of Water Research and Technology (OWRT) review of water quality criteria for reuse lists only one specific organic requirement in connection with general agricultural irrigation.[4] Phenols should be restricted to a maximum concentration of 50 mg/L, quite a high limit. However, when truck crops are involved, a maximum level of 20 mg/L for 5-day BOD is also recommended.

Stipulations with regard to reuse of effluent for landscape irrigation are only slightly greater. The OWRT report found a consensus criterion that oil and grease should be absent for this use--on aesthetic grounds--in addition to the previous phenol and BOD criteria.

Standards for reuse of wastewater effluent in watering of livestock and wildlife are almost equally meager. Phenol, at a maximum of 1000 mg/L, and floating oil, not supposed to be present, are the only specifically listed criteria. However, it is also recommended that pesticide concentrations be less than the corresponding MCLs for drinking water.

For the most part, lack of concern for the trace organic substances that may be present in effluents otherwise suitable for agricultural reuse is a result of the fact that, until now, no damages to crops or livestock have occurred because of the presence of usual concentrations of such compounds. But portions of the water applied for irrigation eventually reach either the groundwater table or surface receiving waters. The organic substances present in the interim may have been oxidized, in which case they are of minor concern, or they may pass through the soil with the remaining water to pollute the groundwater or the receiving stream or they may be absorbed and concentrated in the soil with eventual effects as yet undetermined.

With regard to the current situation, Jones and Lee[16] have made probably the most direct and penetrating remarks in their paper for the conference on health effects of land application of wastewater held in San Antonio in December 1977, stating, "It is presently impossible to assess the risk associated with land disposal of wastewater... containing hazardous chemicals. There is no justification for assuming that land disposal is environmentally less damaging than conventional water disposal practices. Water disposal systems tend to be dispersive and diluting, whereas terrestrial systems concentrate the chemicals in the soil and enhance the opportunity for uptake by biological systems. Terrestrial systems also pose greater risk of groundwater contamination."

The fates of organic chemicals during soil passage of water thus are matters of important concern that need much research and investigation during the coming decade.

Recreational Uses

The primary criterion for recreation water is, of course, hygienic safety or freedom from pathogenic microorganisms. Stipulations relating to organic materials have generally been indirect, expressed in terms of sensory or physiological effects, rather than as specific organic constituents. Thus, virtual freedom from color, odor, oil and scum have been specified by the EPA and other agencies, but no standards for individual organic compounds or even classes of them have been recommended in connection with general recreation. However, two types of organic substances have regulatory limits when fishing or fisheries are involved. Polychlorinated biphenyls (PCBs), which are representative of toxic substances that may bioaccumulate in fish, to be transferred to man, have been limited to 10^{-6} mg/L, and phenols, which are examples of substances that may cause tainting of fish flesh, have a recommended limit of 10^{-4} mg/L. The latter standard, if established, may cause difficulties, because Englande and Reimers have found that currently operating advanced waste treatment systems are unable generally to reduce phenols to less than 10^{-3} mg/L.[17]

Other organic substances, such as aliphatic hydrocarbons in the kerosene range, aromatic hydrocarbons and chlorinated compounds like paradichlorobenzene and chloroanilines will undoubtedly require future consideration with regard to these possibilities.

Industrial Uses

Industrial uses of water are so diverse and the quality requirements are so varied that a single set of criteria is impossible. For use as cooling water, either in power generation or in other industries, the major stated criterion is that there be no floating oil. Otherwise, normal clarified secondary effluent appears suitable. For use as boiler feed, the requirements increase as the operating pressure increases. To feed very high-pressure boilers, 100 atmospheres or greater, carbon-tetrachloride extractable matter should be virtually zero, and detergents should be less than 0.1 milligrams per liter. Otherwise, for this use and also for reuse as process water in most chemical, petroleum, paper, and primary metals industries, the organic composition of clarified secondary municipal effluents seems generally satisfactory as received.

The industries for which specific organic substances are important are those concerned with food, beverages and kindred products. Overall, water of potable quality is required, so that the MCLs relating to organic materials in drinking water apply. In some instances, standards for sensory properties, such as color or organoleptic quality may be even more rigorous. Presumably, however, any water meeting drinking water MCLs would be acceptable for further in-plant treatment.

Groundwater Recharge and Potable Reuse

Reclaimed wastewater intended for groundwater recharge to potable aquifers clearly must meet more restrictive and extensive criteria than those for other types of reuse. As a minimum, compliance with MCLs for drinking water is required. However, some parameters, especially those relating to a number of specific organic substances, need to be limited even more strictly. The particular types of organic substances that need stricter limitation are those that are not degraded in the groundwater, those that may build up in the water during recycle and those that may interact reversibly with the soil during passage into the groundwater.

When recharge is performed by direct injection, then the full organic content of the recharged water impacts on the groundwater aquifer. Moreover, opportunities for subsequent degradation of many organic compounds under the nearly sterile conditions of most aquifers are comparatively limited. Thus, relatively volatile substances like tetrachloroethylene and methyl-chloroform, which would be lost from surface waters by volatilization over a period of time, appear to persist almost indefinitely in confined, underground water. Studies by McCarty and others have shown that these small chlorinated compounds pass quite readily through advanced waste treatment processes.[17] For example, effluent from the advanced waste treatment facility in Orange County--Water Factory 21--contained more than 0.5 micrograms per liter each of trichloroethylene, tetrachloroethylene and methyl chloroform about one-third of the time, and these concentrations were substantially maintained even through reverse osmosis.

When recharge occurs by percolation or infiltration, there is opportunity for reaction of organic matter in the upper soil layers and for removal of organic substances by interaction with soil particles, thus providing for some degree of purification. In the latter instance, however, the retained material, if truly persistent, may later break through into the aquifer, as Roberts and McCarty have shown for substances like chlorobenzene, dichlorobenzenes, benzonitrile and styrene at Palo Alto.[18]

Other organic substances, such as aliphatic hydrocarbons in the kerosene range, aromatic hydrocarbons and chlorinated compounds like paradichlorobenzene and chloroanilines will undoubtedly require future consideration with regard to these possibilities.

Industrial Uses

Industrial uses of water are so diverse and the quality requirements are so varied that a single set of criteria is impossible. For use as cooling water, either in power generation or in other industries, the major stated criterion is that there be no floating oil. Otherwise, normal clarified secondary effluent appears suitable. For use as boiler feed, the requirements increase as the operating pressure increases. To feed very high-pressure boilers, 100 atmospheres or greater, carbon-tetrachloride extractable matter should be virtually zero, and detergents should be less than 0.1 milligrams per liter. Otherwise, for this use and also for reuse as process water in most chemical, petroleum, paper, and primary metals industries, the organic composition of clarified secondary municipal effluents seems generally satisfactory as received.

The industries for which specific organic substances are important are those concerned with food, beverages and kindred products. Overall, water of potable quality is required, so that the MCLs relating to organic materials in drinking water apply In some instances, standards for sensory properties, such as color or organoleptic quality may be even more rigorous. Presumably, however, any water meeting drinking water MCLs would be acceptable for further in-plant treatment.

Groundwater Recharge and Potable Reuse

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For more than 30 years, the Dutch have been recharging treated Rhine river water by infiltrating it into the groundwater aquifers of their coastal dunes. Within recent years, as highly sensitive analytical techniques became available, they have found that numerous persistent organic pollutants, such as dichlorobenzenes, chloroanilines and phthalate esters have penetrated into their groundwaters. They are currently conducting exhaustive studies on the organic materials that may have interacted with and been accumulated by the filtering soils over more than 30 years, to determine both the degree of pollution of the soil and its effects on the soil's characteristics and utility. Results of this study should have a major effect on our knowledge of requisite organic criteria for groundwater recharge.

Recent analyses of concentrates from six advanced waste treatment plants have shown that each contains between 100 and 500 identifiable organic compounds. Each effluent probably also contains a larger number of other unidentified compounds. Discovering which of these need limitation and developing the necessary criteria for all these compounds with regard to different types of reuse is a formidable task for the coming decade. It is also, however, one that must be accomplished, at least for those compounds with high toxicity and great persistence, if potable water reuse opportunities are to be realized with security.

METHODS OF CONTROL OF ORGANIC SUBSTANCES

Two broad alternatives are available to reduce or eliminate organic substances in municipal wastewater intended for reuse. The first is source control of the substances, and the second is treatment for removal. This section is intended as an overview of potential control methods. Detailed reports on organic substance removal by biological processes and physical/chemical processes were discussed earlier in this monograph.

Source Control

Industrial source control is the reduction or elimination of the discharge of pollutants to municipal collection systems, a very effective way of improving the quality of reclaimed water, especially for municipal facilities not designed to remove specific organic substances. By in-plant recycling of flows that would otherwise be discharged, the net amount of water that needs to be treated to meet these strict standards is reduced.

Another major incentive toward source control is the recovery of materials with value. The realization by industry that "waste" by-products represent a potential source of revenue to offset production costs has led to the decrease of industrial discharges. The cost of water itself has compelled industry to conserve and recycle water, which reduces pollutant discharges to municipal systems. This trend is expected to continue, as water costs escalate, energy costs increase, and stricter water-quality standards necessitate costlier treatment of wastewater.

Treatment

Not many municipal wastewater-treatment facilities are designed to remove synthetic organic substances. This section provides a brief overview of the capability of selected treatment processes to reduce the concentrations of such organic substances. These processes have been used at several advanced wastewater treatment facilities where water reclamation is practiced.

Lime Treatment—

Lime is used for removing phosphate from wastewater. If the pH is raised to about 11.5, the effluents produced exhibit nearly total phosphorus removal and BOD and

COD reductions in the range of 65 to 80 percent.[19] Most of the BOD and COD reduction is due to coagulation and adsorption of the suspended and colloidal organic matter by the calcium carbonate and magnesium hydroxide precipitates. Soluble BOD and COD in the form of organic acids also are removed by precipitation of their calcium salts.

Studies at Water Factory 21, Orange County, California give a comprehensive overview of organic removal achieved by lime and other treatment processes.[20] Table 3 shows trace organic removals during two periods representing different influent conditions. Some removal of pesticides, phthalates and PCBs was recorded during lime treatment. Removals were somewhat higher when trickling-filter effluent was used as a feed because of higher initial solids concentrations and higher proportions of industrial wastes, which resulted in higher concentrations of the organic substances themselves. Many other trace organic substances were not reduced during lime treatment, especially when better quality wastewater was fed to the facility. The lime treatment effluent may have been contaminated, which would account for the concentration increases. Firm conclusions cannot be drawn for these substances because of the large statistical range for the 95-percent confidence interval, but lime treatment, in general, can be characterized as relatively ineffective for removal of trace organic substances.

Activated Carbon Adsorption—

Residual dissolved organic compounds from secondary-treatment plant effluents can be effectively removed by either granular or powdered activated carbon. Treated COD values of less than 10 mg/L are possible when the COD of the secondary effluent is in the range of 50-150 mg/L. Carbon adsorption is more effective for large nonpolar organic molecules than for smaller or more polar compounds.

If aerobic conditions are maintained in a granular carbon bed or in a fluidized suspension of powdered carbon, the biological degradation of adsorbed organics, unless they are totally refractory, can be accomplished with resultant *in situ* partial regeneration of the carbon. Apparently, the presence of activated carbon in an aerobic biomass, such as activated sludge, can enhance the biodegradation of organics that are difficult or slow to biodegrade. The organics that are completely refractory remain adsorbed on the carbon and are removed with the carbon, which can be heat-regenerated.[21,22]

If the wastewater effluent is contacted with ozone ahead of a granular carbon bed, many of the complex nonbiodegradable organic compounds are broken down to simpler compounds which are adsorbed and biodegraded in the carbon bed, and the bed will be maintained in an aerobic condition as a result of the pre-ozonation.[23]

Removals of organic materials by granular activated carbon at Water Factory 21 are shown in Table 4. Chlorinated benzenes, phthalates, aromatic hydrocarbons and brominated trihalomethanes were removed as effectively as COD. Breakthrough of COD, TOC and trihalomethanes occurred at regular intervals, indicating a need for carbon regeneration. According to McCarty et al.[20], when granular activated carbon is being used to maintain low concentrations of trihalomethanes, COD, or TOC, regeneration must be done more frequently than when only more hydrophobic materials (e.g., pesticides and PCBs) are being controlled.

Air Stripping—

At Water Factory 21, air stripping has been highly effective for removal of many trace organic contaminants.[24] Table 5 indicates that the chlorinated benzenes and the halogenated methanes, ethanes, and ethylenes are effectively removed.

Volatile compound removals were also recorded in decarbonators that follow reverse osmosis units. Originally, these removals were attributed to the reverse osmosis unit itself. Seventy percent or greater removals of bromodichloromethane, chloroform, dibromochloromethane, and tribromomethane have been achieved.

Table 3. Removal of Trace Organic Substances by Lime Treatment at Water Factory 21.

Contaminant	With Trickling Filter Influent Second Period			With Activated Sludge Influent		
	Inf. Conc. µg/L	Eff. Conc. µg/L	% Removal (95% CI)	Inf. Conc. µg/L	Eff. Conc. µg/L	% Removal (95% CI)
Di-n-butyl phthalate				0.79	0.23	71 (-80 to 95)
1,2,4-Trichlorobenzene	0.46	0.22	52 (-96 to 88)	0.11	0.035	68 (2 to 90)
Bis-(2-diethylhexyl)-phthalate				11	3.8	65 (32 to 82)
Lindane				0.14	<0.05	>64
1,3-Dichlorobenzene	0.68	0.12	82 (15 to 96)	0.16	0.10	38 (10 to 57)
Dimethylphthalate				4.8	3.1	35 (-5 to 60)
Diisobutylphthalate				4.7	3.2	32 (12 to 48)
1,4-Dichlorobenzene	2.1	1.02	51 (-7 to 78)	1.85	1.29	30 (16 to 42)
PCBs as Aroclor 1242				0.47	0.37	21 (-15 to 46)
1,2-Dichlorobenzene	2.4	1.2	50 (-71 to 85)	0.64	0.56	12 (-54 to 50)
2-Methylnaphthalene				0.01	0.009	10 (-253 to 77)
Bromodichloromethane	0.09	0.21	-133 (-1340 to 62)	0.53	0.56	-6 (-33 to 16)
Chlorobenzene	2.5	3.0	-20 (-174 to 47)	0.14	0.15	-7 (-80 to 36)
Dibromochloromethane				0.69	0.79	-14 (-42 to 8)
Trichloroethylene	0.9	0.21	77 (-19 to 95)	0.74	0.86	-16 (-270 to 63)
Heptaldehyde				0.10	0.12	-20 (-132 to 38)
Naphthalene	0.57	0.21	63 (-22 to 89)	0.033	0.041	-24 (-548 to 76)
Chloroform	1.6	1.09	32 (-26 to 63)	3.2	4.1	-30 (-79 to 5)
1,1,1-Trichloroethane	4.7	0.94	80 (-30 to 97)	3.3	4.7	-45 (-198 to 30)
Tetrachloroethylene	0.6	0.16	73 (10 to 92)	1.67	2.5	-50 (-141 to 7)
p-Xylene				0.015	0.023	-53 (-206 to 23)
Ethylbenzene	1.4	0.23	83 (62 to 93)	0.043	0.067	-56 (-202 to 20)
Styrene				0.048	0.076	-58 (-294 to 36)
Tribromomethane				0.40	0.67	-68 (-143 to -15)
1-Methylnaphthalene				0.008	0.019	-138 (-510 to 8)
m-Xylene				0.035	0.086	-146 (-329 to 41)

Table 4. Removal of Organic Materials by Granular Activated Carbon at Water Factory 21

	With Trickling Filter Influent			With Activated Sludge Influent		
Contaminant	Inf. Conc.	*Eff. Conc.	% Removal (95% CI)	Inf. Conc.	Eff. Conc.	% Removal (95% CI)
COD	42	16.6	60 (58 to 63)	24	12.3	59 (46 to 52)
TOC	14	7.0	51 (48 to 54)			
1,4-Dichlorobenzene	0.02	0.02	17 (-750 to 90)	0.07	0.001	98 (43 to 100)
1,2-Dichlorobenzene	0.17	0.03	82 (0 to 97)	0.02	0.002	91 (-150 to 100)
Diisobutylphthalate				2.0	0.27	87 (61 to 95)
Tribromomethane				0.41	0.08	81 (40 to 94)
Dimethylphthalate				1.3	0.47	64 (24 to 83)
Chlorobenzene/o-xylene	0.09	0.05	46 (-5 to 72)	0.11	0.04	63 (30 to 80)
Bromodichloromethane	4.8	1.3	72 (46 to 86)	1.8	0.81	54 (5 to 77)
Dibromochloromethane	1.4	0.23	84 (58 to 94)	0.65	0.31	52 (2 to 77)
m-Xylene				0.05	0.023	50 (7 to 73)
Naphthalene				0.05	0.023	50 (-8 to 76)
Di-n-butylphthalate				0.59	0.33	44 (-90 to 84)
Carbon tetrachloride				0.07	0.0	20 (-110 to 70)
Ethylbenzene	0.06	0.03	45 (3 to 69)	0.02	0.019	17 (-77 to 61)
Bis-(2-ethylhexyl)-phthalate				3.4	3.1	9 (-69 to 51)
Tetrachloroethylene	0.04	0.01	72 (-260 to 98)	0.16	3.1	-6 (-190 to 61)
Methylene chloride	1.5	1.6	-7 (-98 to 43)			
1,1,1-Trichloroethane				0.16	0.018	(-430 to 76)
2-Methylnaphthalene				0.07	0.02	-18 (-150 to 45)
Chloroform	8.2	6.7	21 (-70 to 63)	5.	7.5	-41 (-146 to 19)

*Geometric mean conc. in μg/L except TOC and COD which are in mg/L.

Table 5. Removal of Trace Organic Substances by Air Stripping at Water Factory 21

	With Trickling Filter Influent			With Activated Sludge Influent		
Contaminant	Inf. Conc. μg/L	Eff. Conc. μg/L	% Removal (95% CI)	Inf. Conc. μg/L	Eff. Conc. μg/L	% Removal (95% CI)
Tetrachloroethylene				2.5	0.13	95 (88 to 98)
1,4-Dichlorobenzene	1.0	0.03	97 (88 to 99)	1.3	0.10	92 (89 to 94)
1,1,1-Trichloroethane	0.94	0.09	90 (0 to 99)	4.7	0.43	91 (76 to 96)
1,2-Dichlorobenzene	1.2	0.18	85 (-10 to 98)	0.56	0.07	88 (61 to 96)
Tribromomethane				0.67	<0.1	>85 —
Heptaldehyde				0.12	<0.02	>83 —
1,3-Dichlorobenzene	0.12	0.02	83 (-46 to 98)	0.10	0.02	83 (60 to 93)
Bromodichloromethane	0.21	0.08	62 (-320 to 97)	0.56	<0.1	>82 —
Dibromochloromethane				0.79	0.14	82 (76 to 87)
Chloroform	1.1	0.18	83 (70 to 91)	4.1	0.88	79 (64 to 87)
Trichloroethylene	0.21	0.013	94 (-73 to 100)	0.86	<0.2	>77 —
Styrene				0.076	0.037	51 (-180 to 92)
1-Methylnaphthalene				0.019	0.011	42 (-170 to 88)
1,2,4-Trichlorobenzene	0.22	0.11	50 (-440 to 95)	0.035	0.02	40 (-290 to 91)
Ethylbenzene	0.23	0.10	57 (-110 to 91)	0.067	0.041	39 (-58 to 76)
Diisobutylphthalate				3.2	2.3	28 (-1 to 49)
Chlorobenzene/o-Xylene	3.0	0.11	96 (89 to 99)	0.15	0.11	27 (-46 to 64)
m-Xylene				0.086	0.07	19 (-84 to 64)
Naphthalene	0.21	0.18	14 (-257 to 79)	0.041	0.37	10 (-840 to 91)
Dimethylphthalate				3.1	2.8	10 (-79 to 54)
PCB as Aroclor 1242				0.37	0.36	3
2-Methylnaphthalene				0.009	0.009	0 (-740 to 88)
Heptylcyanide				0.047	0.048	-2 (-160 to 60)
p-Xylene				0.023	0.031	-35 (-200 to 39)

Reverse Osmosis—

Filtered secondary-treatment effluents having COD values of about 30 mg/L can have this parameter reduced to less than 5 mg/L by reverse osmosis.[25] At Water Factory 21, COD decreased from 14.6 to 1.3 mg/L (91 percent reduction) during reverse-osmosis (RO) treatment. Because membrane fouling by organic matter is a problem, a program of membrane cleaning is required when soluble and colloidal organic material is removed in a RO system. Reverse osmosis is not effective in the removal of many low-molecular-weight trace organic contaminants, as shown in Table 6, which is based on a pilot unit at Water Factory 21.

Chlorination—

Very few soluble organic substances are removed completely by chlorination. Although chlorine-substituted products are not known to be formed from more than 3% to 5% of the applied chlorine, the toxicities and biological inertness of many chlorinated compounds may render chlorinated wastewaters potentially more harmful from a chemical point of view than non-chlorinated ones.[26,27,28] Thus, although chlorination is used regularly to reduce levels of pathogenic organisms in wastewater effluent, it tends to exacerbate rather than alleviate the problem of organic compounds in waters intended for reuse.

Ozonation—

Ozone can oxidize many organic structures and thus accomplish partial reduction in ultimate COD and BOD. It is used principally to reduce the concentration of organic matter following secondary treatment and filtration, but it can be used in conjunction with carbon columns for removal of partially oxidized organic substances. Ozone breaks down many complex organic compounds to simpler structures which can then be readily biodegraded. Actually, most of the reactions of ozone with organic pollutants in wastewater are of this type. The specific reaction chemistry between organic substances in water and ozone is quite complex and not completely defined. Apparently, some intermediate ozonides are formed that may have certain toxic properties, but they appear to be quite unstable.[26] Many types of organic compounds, such as aliphatic hydrocarbons, primary alcohols, carboxylic acids and chlorinated hydrocarbons are resistant to ozone treatment and so cannot be removed by normal ozonation.

Ozone may also be used in combination with ultraviolet light. A U.S. Army study indicated that UV light catalyzed the oxidation of refractory organic materials by ozone.[29]

PRESENT PROBLEMS AND FUTURE OUTLOOK

An Assessment of Present Problems

During the 1970s, construction of municipal wastewater-reuse projects increased tremendously. Two problems, however, have constrained the potential utilization of reclaimed water. These interrelated problems are: a lack of monitoring and testing techniques and the lack of standards for various types of reuse. Both of these problems are connected with the presence of organic substances in wastewater.

Monitoring and recording of plant-process performance and sustained high reliability are imperative conditions for most reuse applications. Some reclamation facilities have redundant process trains or the ability to recirculate or discharge water that does not meet use criteria. Reuse would be greatly enhanced if there were fast, inexpensive testing procedures by which organic substances and pathogens could be identified in the product water. Health agencies in many states have taken very conservative positions on certain types of reuse applications because of the possibility that periodic upsets in treatment would result in the utilization of

Table 6. Removal of Contaminants by Pilot Reverse Osmosis Systems at Water Factory 21

Contaminant	Inf. Conc. μg/L	Eff. Conc. μg/L	% Removal (95% CI)
Chloroform	5.5	5.5	0(-51 to 34)
Bromodichloromethane	0.87	0.95	-9(-72 to 31)
Dibromochloromethane	8.82	0.91	-11(-41 to 13)
Tribromomethane	0.63	0.65	-3(-61 to 34)
1,1,1-Trichloroethane	4.9	6.3	-28(-151 to 35)
Trichloroethylene	1.5	1.7	-12(-118 to 42)
Tetrachloroethylene	1.5	1.8	-21(-79 to 18)
Chlorobenzene	0.14	0.07	49(-18 to 78)
1,2-Dichlorobenzene	0.46	0.38	17(-72 to 60)
1,3-Dichlorobenzene	0.12	0.065	46(10 to 67)
1,4-Dichlorobenzene	1.2	0.99	17(-9 to 37)
1,2,4-Trichlorobenzene	0.04	0.11	-150(-541 to 3)
Heptaldehyde	0.18	0.05	71(39 to 86)
Heptylcyanide	0.04	0.02	49(-90 to 86)
Ethylbenzene	0.05	0.029	44(-66 to 81)
m-Xylene	0.08	0.045	45(-67 to 82)
p-Xylene	0.02	0.022	8(-236 to 75)
Naphthalene	0.05	0.067	-31(-865 to 82)
1-Methylnaphthalene	0.02	0.02	5(-191 to 69)
2-Methylnaphthalene	0.02	0.02	-19(-264 to 61)
Styrene	0.02	0.01	44(-373 to 93)
Dimethylphthalate	1.3	1.0	19(-47 to 56)
Diethylphthalate	0.45	0.52	-16(-168 to 50)
Di-n-butylphthalate	0.69	0.73	-6(-194 to 62)
Diisobutylphthalate	2.9	2.5	14(-22 to 39)
Lindane	0.08	0.06	27(0 to 47)

reclaimed water of unacceptable quality. Present monitoring methods for several important parameters take too long to make in-plant process changes before discharge occurs.

An example of the wide variation of reuse standards is found in comparing standards for irrigation of golf courses set by the California Department of Health Services with those of the State of Arizona. California's Title 22 criteria call for an oxidized, disinfected effluent meeting a bacterial concentration of 22 coliforms per 100 ml. A similar project in Arizona would require only that the effluent contain a monthly average of no more than 5,000 coliforms per 100 ml.

For nearly all nonpotable reuse activities, the principal health concern has been the presence of pathogenic organisms and the degree of control needed to reduce risks. For some types of nonpotable uses, the question of organic substances is also very important and requires further study.

EPA has recognized the constraints imposed on reuse by the lack of sound standards. A national conference in July 1980 examined protocol for the development of both potable and nonpotable reuse standards.[30] Some of the conclusions reached were:

- A single set of water quality standards should apply at the tap, regardless of the source of the raw water.
- Additional information is needed for raw water coming from highly polluted sources in order to treat it properly.
- The most difficult and as yet unanswered question is associated with health effects. New parameters are needed to deal with organic compounds in drinking water.
- A broader spectrum of indicator organisms and disinfectants may be required to deal with pathogens and their toxins.
- Scientists are unable to predict the transport and transformation of metals, organics, and biological substances in groundwater.

Overview of Current Research Efforts

Current research efforts in reuse of municipal wastewater in the United States are a continuation of studies made in the late 1960s and early 1970s. Foreign research has been concentrated primarily in Israel and South Africa. Research efforts can be broadly classified as process and nonprocess.

In the 1970s, major EPA-sponsored process research projects included the experimental plants at Blue Plains, Washington, D.C., Orange County, California Water Factory 21 and the Los Angeles County Sanitation District's Facility in Pomona. Other federal agencies involved in reuse are the Department of the Interior, Office of Water Research and Technology, the Department of Agriculture, and the Army Corps of Engineers. Many of the reuse projects shown in Table 1 are furnishing valuable information useful to other municipalities considering reuse.

A major potable-reuse research effort is being sponsored by EPA, OWRT and the Denver, Colorado Water Board. A 1-mgd advanced wastewater treatment facility will produce reclaimed water from secondary effluent for possible potable reuse in the City of Denver. Denver is the only city in the U.S. pursuing a major direct potable-reuse program. However, several other cities have demonstrated or are planning groundwater recharge with reclaimed water. In some cases, the groundwater basins are used for potable purposes.

Many of the process-related research projects of the last ten years have resulted from stringent EPA effluent-discharge regulations. The effluents produced at these facilities have been of too high a quality simply to dispose of. At many major reuse facilities, the incentive for reuse was to either avoid high treatment requirements for discharge or to better utilize a good quality product water.

Nonprocess research has been carried out by many agencies including EPA's Municipal Environmental Research Laboratory (MERL) and Health Effects Research Laboratory (HERL). A major MERL effort is a "Guidelines for Water Reuse" manual that addresses a broad range of the technical, economic, and institutional issues faced by water/wastewater managers planning municipal wastewater reuse systems.[1] Major health studies have focused on the obvious hazards associated with bacterial and viral contaminants, as well as on the long-term effects of small quantities of organic compounds.

OWRT has sponsored several studies dealing with the social, legal and institutional aspects of reuse. Public acceptance surveys have been conducted in many areas of the country. Several studies point out that public officials have lagged behind the public in their assessment of public opinion on reuse.[31]

Compilation and dissemination of information on reuse activities is carried out by several agencies including the American Water Works Association (AWWA) Research Foundation. The Foundation sponsored a water reuse conference in 1979 that attracted over 160 speakers. A three-volume set of conference proceedings is a significant source of useful information. The research foundation also publishes a monthly "Municipal Wastewater Reuse News." A major reuse research symposium held in 1975 was sponsored by EPA, AWWA, and Water Pollution Control Federation (WPCF). Entitled "Research Needs for Potable Reuse of Municipal Wastewater" the workshop reached these principal conclusions:

1. The identified needs pertain to indirect wastewater reuse as well as possible direct potable reuse.
2. Identification of contaminants in present drinking waters and the development of optimum control processes is urgent.
3. Development of rapid, sensitive, and accurate testing procedures for all types of contaminants and establishment of on-line continuous monitoring where required.
4. Toxicological studies using *in vitro* screening and testing are of high priority.
5. Long-term health effects of reuse involving retrospective and prospective epidemiological surveys of populations exposed to indirect wastewater reuse should be undertaken as an international collaborative activity.
6. Improved exchange of information relative to reuse is needed here and abroad. One potential coordinating body in existence is the World Health Organization International Reference Centre for Community Water Supply located at The Hague.

Future of Reuse

Municipal reuse planning of the last decade was based on projected long-term water shortages. Reuse projects can free up for potable use the limited high-quality sources of water in communities, while assuring sufficient quantities of water of adequate quality for industrial, agricultural, and other uses. In the future, municipal water-supply planning will involve the tailoring of different qualities of water to users' needs.

A study completed in 1979 for OWRT, projected that reuse would undergo a seven-fold increase by the year 2000, growing from about 680 millions of gallons per day to 4,750 millions of gallons per day.[4] Reuse would be centered largely in agricultural irrigation and industrial cooling.

This expected increase in reuse will require closer scrutiny of the impact of organic materials in reclaimed water. Since potable reuse will only make up a very small portion of the total demand, research on organic substances will not receive a large portion of the research spending. Nevertheless, for those municipalities investigating potable reuse, health effects of long-term ingestion of small amounts of organic substances need to be studied carefully. Other types of reuse projects involving high water-quality standards--such as irrigation of specific food crops--will also necessitate an examination of organic substances in reclaimed water.

As reuse projects become more common, planning will become more sophisticated. Because reuse usually involves marketing of reclaimed water, its success in each case depends on establishing a working relationship between the water purveyor and potential reclaimed-water user. The future of reuse will be closely intertwined with the rethinking of the traditional, separate roles of water and wastewater management and greater attention to institutional matters.

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MANAGEMENT OF RESIDUALS SEPARATED FROM MUNICIPAL WASTEWATER

Richard I. Dick

INTRODUCTION

A common feature of nearly all processes used for treatment of municipal wastewaters is that they are intended to remove contaminants in the form of suspended solids. If a constituent that is to be removed does not exist as particulate matter, then chemical, physical, or biological means are used to make the constituent a part of a particle that can be removed by solids-liquid separation procedures. As a result of this approach, residues from municipal wastewater treatment consist of suspensions of particles in water. The residue is called "sludge," and its management is a major challenge and expense in environmental quality control.

Contaminants that are associated with settleable solids in the raw wastewater can be removed in primary sedimentation processes without the need for prior treatment. In the past, primary sedimentation often was the only form of wastewater treatment provided for municipal wastewaters. At present, primary treatment ordinarily is provided prior to more extensive secondary wastewater treatment.

When wastewater constituents that are to be removed do not arrive at the treatment plant in association with suspended solids, then treatment processes are used to produce suspended solids containing the contaminant. These solids are then removed by solids-liquid separation processes (commonly sedimentation) to effect removal of the contaminant. Chemical precipitation of phosphorus offers an illustration of a chemical process for converting a soluble material (orthophosphate) into an insoluble form (typically phosphorus in association with iron, aluminum, or calcium) so as to achieve removal.

Biological processes for removing organic material from wastewater are, in effect, techniques for biological precipitation of organic material. While some organic material is oxidized to carbon dioxide and lost as a gas, the microorganisms in wastewater treatment processes oxidize only enough organic material to obtain the energy required to synthesize new microorganisms. These organisms are, effectively, the precipitated organic material removed from the wastewater. Because of the usual flocculent nature of the microorganisms, they agglomerate into particles amenable to separation by sedimentation or filtration.

There are a few exceptions to the usual rule that constituents removed from municipal wastewaters are removed in the form of suspended solids to yield sludges. One exception is organic constituents with sufficiently low vapor pressure to be lost

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to the atmosphere as a gas during the process of treatment. In the case of adsorption using granular media such as activated carbon, removal occurs by association with a solid phase, but not in the form of a sludge. Disinfection is another example of a municipal wastewater treatment process that does not produce a particulate residue. Other examples are processes (like ion exchange and reverse osmosis) that produce a concentrated brine--these processes, however, are not in common use in municipal wastewater treatment.

General Characteristics of Municipal Wastewater Treatment Plant Sludges

All wastewater constituents removed in the course of conventional municipal wastewater treatment, excepting those lost by oxidation and volatilization, are contained in wastewater treatment plant sludges. Inasmuch as the ultimate removal mechanism for these materials is solids-liquid separation, the contaminants exist primarily in the solid phase. The substantial liquid phase of sludges is derived from the wastewater, and, hence, sludges also contain materials not preferentially removed in wastewater treatment. The chemical properties of municipal wastewater sludges can best be characterized as being heterogeneous and variable. Chemical characteristics of sludges are highly dependent upon industrial contributions to municipal wastewater treatment systems. Not all adverse chemical properties of sludges can be attributed to industries, however[1].

Conventionally, municipal wastewater treatment plants have not been designed specifically to remove toxic organic compounds; they have been designed primarily to remove suspended solids contained in raw wastewater and organic compounds that are biologically degradable. Occasionally, especially in recent years, designs have also been developed to include removal of the nutrients phosphorus and nitrogen. Additionally, disinfection processes for inactivation of microorganisms and viruses are common.

While municipal wastewater treatment plants are not currently designed specifically to remove toxic organic chemicals contained in municipal wastewater, appreciable removal occurs[2]. This incidental removal of toxic organic compounds is caused by mechanisms such as volatilization, adsorption, absorption, and chemical or biological oxidation (see chapter in the Monograph by Irvine). Aside from those organic compounds lost by volatilization and oxidation, the organic materials removed from wastewater would be expected to be contained in the solid phase of the sludge. It is important to recognize, however, that even if no preferential association of toxic organic compounds with a solid phase of sludge occurred, toxic organics in wastewaters would still be included in sludges. This is because the compounds would be in the liquid phase of the sludge which typically represents about 95 percent of the volume of sludges generated in primary treatment and about 99 percent of the volume of sludges produced by secondary wastewater treatment.

Sludges from biological wastewater treatment consist principally of excess organisms synthesized in wastewater treatment. Additionally, a high degree of removal of the many pathogenic organisms and viruses contained in municipal wastewaters occurs during wastewater treatment, and, hence, such organisms and viruses are found in sludges. The organisms in sludge that may be pathogenic to humans include many species of bacteria, protozoa, and helminths (worms) together with human viruses.

The physical properties of municipal wastewater treatment plant sludges are complicated by the fact that the solid phase of sludges is comprised of assemblages of flocculent particles. Many of the particles in sludges are hydrophilic, and significant amounts of water are oriented to the surface of the particles. As particle agglomeration occurs, additional water is entrained. Because of the high water content of the agglomerated particles, their specific gravity may be barely greater than one. This leads to poor settleability and accounts for the dilute suspended solids content of typical municipal wastewater treatment plant sludges. A further complication of the physical structure of sludges is that when a pressure gradient is applied in an attempt to remove the excessive moisture in sludges so as to reduce sludge volume, the loose flocculent structure tends to deform creating a highly impermeable matrix through which movement of moisture is impeded.

Nature and Magnitude of Municipal Sludge Management

Traditionally, the focus of water pollution control activities has been on the processes used to treat wastewater. Yet, roughly half of the overall cost of wastewater management is for management of the residues (sludges) produced by wastewater treatment. Furthermore, the complexity and cost of responsible residue management has kept pace with the cost and complexity of processes needed to achieve higher degrees of water pollution control. When primary wastewater treatment plants are converted to secondary plants, for example, the mass of residual sludge is nearly doubled (on a dry solids basis), the volume of wet sludge is more than doubled (because of the high moisture content of secondary sludges), and the cost of sludge management is escalated significantly (because of the typical adverse physical properties of secondary sludge). Similarly, the need for phosphorus removal at some wastewater treatment plants (to control eutrophication of receiving waters) has severe implications in sludge management.

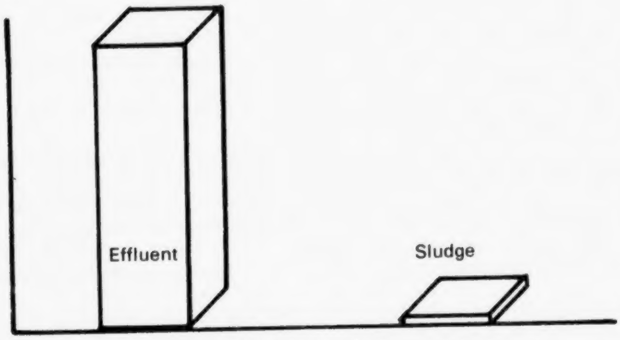
Secondary wastewater treatment produces in the order of 0.1 kg of residual solids (on a dry basis) per capita per day. Regrettably, the sludge does not consist of dry solids, but, rather, as has been noted, it is a very dilute aqueous suspension of solids. At a typical average moisture content of about 3 percent by weight (for a mixture of primary and secondary sludge), the total mass of residual material per person exceeds 3 kg/day. The relative quantities of treated effluent and sludge and the comparative costs of wastewater treatment and sludge management are illustrated further in Fig. 1.

Estimates of total municipal sludge production analyzed by a committee of the National Academy of Sciences[3] indicated that current (1982) annual production is about seven million tons (about 6.3 million metric tons) on a dry solids basis. Estimated municipal production in 1990 is nearly ten million tons (nine million metric tons). This represents a twofold increase since 1972.

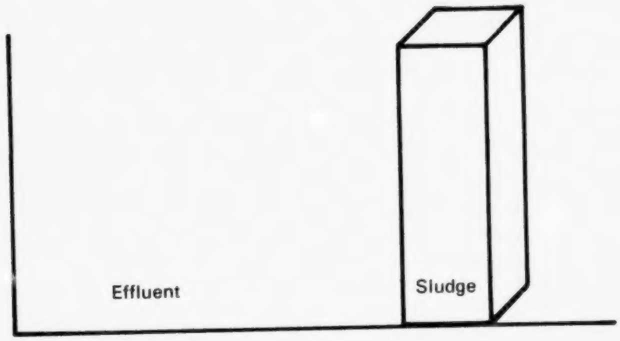
The opportunities for ultimate discharge of the residues remaining after treatment of municipal wastewaters are extremely limited. They can be reclaimed or disposed to air, land, or water--no other alternatives exist. A wide variety of processes have been developed to treat sludges so as to prepare them for one of these possible means for reuse or disposal. In later sections of this chapter, processes used in municipal sludge treatment are described and reclamation and disposal possibilities are considered in more detail. Because of the focus of this book on organic compounds (particularly priority pollutants) in water and wastewater, special attention is given to the fate of organic compounds in processes for municipal sludge treatment and in the environment. In addition, available information on the effects of organic compounds in sludge on the performance of sludge treatment processes and on the environment is reviewed.

CHEMICAL COMPOSITION OF MUNICIPAL SLUDGE

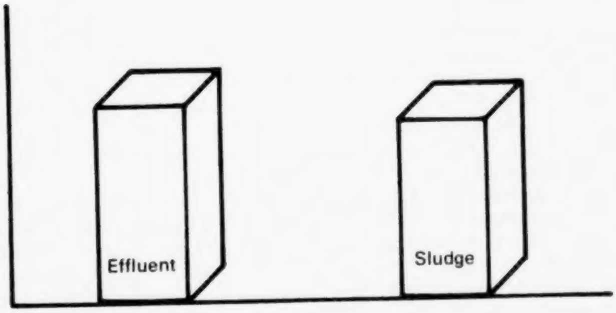
The composition of sludges produced by municipal wastewater treatment is as complex and diverse as the activities served by the wastewater collection system. Even in the absence of industrial wastewater discharges, municipal sludges are highly heterogeneous and difficult to characterize. Municipal sludge characteristics described herein are for "typical" municipalities with some commercial and industrial activities. It must be emphasized that the chemical composition of any particular municipal wastewater sludge could vary widely from the composition described here.



a. Daily Production



b. Potential Annual Accumulation



c. Cost

Figure 1. Relative quantities of treated effluent and sludge and the comparative costs of wastewater treatment and sludge management.

Organic Chemical Constituents of Sludges

Human wastes are a prominent source of wastewater treated at municipal treatment plants, and the sludge produced by conventional treatment processes contains large amounts of microbial mass. Accordingly, typical municipal sludges contain an abundance of common and comparatively inoffensive organic compounds. Indeed, approximately 70 percent of the solids in typical municipal sludges are comprised of organic matter.

Some of the major categories of organic compounds in primary and secondary sludges as reported by Rudolfs and Gehm[4] are shown in Table 1. The high protein content of activated sludge is noteworthy. Furthermore, the essential amino acids are well represented[a][*] in the protein[5]. In addition to the naturally occurring organic compounds found in abundance in sludges, trace quantities of growth factors and vitamins also are present[6]--indeed, vitamin B_{12} has been extracted from activated sludge[7].

The naturally occurring organic compounds that constitute the predominant part of the solid phase of municipal sludges are readily biodegradable, and, hence, could cause oxygen depletion and odors when sludges are returned to the environment. As described in sections that follow, biological stabilization is a common method of sludge treatment to control possible adverse environmental impact from such organic compounds in sludge. The product of biological stabilization still contains large amounts of natural organic materials (often about 50 percent by weight of dry solids), but they degrade far more slowly than the organic compounds in untreated sludges.

In recent years it has become clear that, in addition to the wide assortment of naturally occurring organic compounds, typical municipal sludges also contain a number of synthetic organic chemicals of possible health significance. Limited available data suggest that many such compounds are ubiquitous in the environment and should be expected to be present in any municipal sludge, even though there is no reason to associate the compound with the municipality and, indeed, even if production of the compound has ceased[8].

Limited available data on polychlorinated biphenyl (PCB) concentrations in municipal sludges serve to illustrate the ubiquity of recalcitrant organic compounds in municipal sludges. While exceptionally high PCB concentrations have been found in some municipal sludges (for example, 352 mg/kg of dry solids at Bay City, Michigan[9] and 1,700 mg/kg at Bloomington, Indiana[10]), some PCB's seem to be present in all municipal sludges. In their survey of 16 American cities, for example, Furr, et al.[11] found PCB's even in sludge from a wastewater treatment plant which received almost entirely domestic wastes. Similarly, Epstein and Chaney[9] reported that a Michigan Water Resources Commission study showed PCB's in sludge from each of ten Michigan wastewater treatment plants surveyed (excluding Bay City, concentrations ranged from 0.1 to 32 mg/kg). Lawrence and Tosine[8], who surveyed PCB concentrations at wastewater treatment plants in Ontario, noted that effluents were relatively free of PCB's and that high PCB concentrations in sludges "clearly indicate the ultimate fate of PCB's in treatment plants."

Data on the presence of other organic priority pollutants in municipal wastewater sludges are even more limited than PCB data. However, as might be expected, the data suggest that many organic priority pollutants are typical constituents of ordinary municipal sludges. Furr, et al.[11], for example, found dieldrin to be a common constituent in sludges from 16 municipal wastewater treatment plants surveyed, and Jones and Lee[12] tabulated reported data on 16 different specific pesticides indicating that they are common constituents of domestic sludges.

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[*] Lower case superscripts designate notes listed at the end of this chapter.

Table 1. Major Conventional Organic Constituents in Municipal Sludge*

Primary Constituent	Primary Sludge	Activated Sludge
Grease and fat	7-35	3-17
Cellulose and hemicellulose	7	7
Lignin	5.8	**
Protein	22-28	32-41

*In percent by weight of dry solids
**Included with cellulose and hemicellulose

DeWalle, et al[1] monitored the fate of 36 organic priority pollutants in three municipal wastewater treatment plants. On the average, about 50 percent removal occurred in primary treatment and an additional 60 percent removal of remaining organic material occurred in secondary treatment. Removal was attributed primarily to association of the trace organics with solids, and, hence, they would be incorporated in sludges. In related studies, DeWalle and Chian[13] identified 67 organic priority pollutants at three different treatment plants and detected most of the compounds in sludge. Even some of the volatile organic compounds were concentrated in sludge due to adsorption on solids.

Current ability to predict the amounts of organic priority pollutants to be found in sludge from specific communities is limited. DeWalle, et al[1] anticipated that industrial wastewater pretreatment would be effective in controlling chlorinated solvents, chlorinated and alkyl benzenes, and phenols, but not phthalates. Ramanathan, et al[14] concluded that it currently is not feasible to predict sludge characteristics as they relate to toxic organic substances.

Inorganic Chemical Constituents of Sludges

While emphasis in this monograph is on organic chemicals, it is appropriate to briefly consider major inorganic constituents also. Inorganic constituents influence sludge treatment, utilization, and disposal practices, and, hence, affect the fate and behavior of organic constituents in sludges.

Municipal sludges contain appreciable concentrations of the nutrients nitrogen and phosphorus[6]. Biological sludges are rich in nutrients, but even mixed primary and biological municipal sludges may have nitrogen and phosphorus contents in the order of 3 to 5 percent by weight of dry solids. As compared to commercial inorganic fertilizers, municipal sludges ordinarily contain inadequate amounts of potassium in relation to nitrogen and phosphorus. Appreciable solubilization of nitrogen and phosphorus occurs during anaerobic digestion and, depending upon the amount of liquid removed after digestion, substantial amounts of the nitrogen and phosphorus in sludges may be recycled back to the wastewater treatment processes.

Heavy metals are other inorganic constituents of sludges and they are of concern because of possible entry into the food chain. While industries can be major contributors of heavy metals and source control and pretreatment can significantly reduce their concentration in municipal sludges, heavy metals are found even in purely domestic sludges[15].

Median heavy metal concentrations in sludges from 57 wastewater treatment plants in Michigan[16] were: 12 mg/kg cadmium, 380 mg/kg chromium, 700 mg/kg copper, 52 mg/kg nickel, 480 mg/kg lead, and 2,200 mg/kg zinc (all on a dry solids basis). Values far from these median concentrations were observed at specific cities, however.

SLUDGE TREATMENT PROCESSES

Almost inevitably, sludges produced by municipal wastewater treatment are treated prior to being reclaimed or disposed of. Appropriately, the type of treatment provided varies widely depending upon local circumstances. The purpose of treatment processes is either to remove liquid from sludge or to alter sludge quality[17]. Sludge volume reduction is often associated with both types of treatment. Some sludge treatment processes in the two treatment categories are described in the sections that follow.

Processes for Removing Water from Sludge

The moisture content of municipal sludges has a significant effect on the cost and performance of most processes for sludge treatment, utilization, and disposal. The performance of an anaerobic digester (see following section), for example, depends on the length of time organic solids are retained. Thus, if the volume of sludge to be anaerobically digested is reduced by 50 percent by removal of water, the volume of the digester can be reduced by the same fraction, and capital costs can be significantly reduced. Similarly, the cost of facilities for storing and transporting sludge is highly dependent upon the amount of water with which the sludge solids are associated. Economical performance of sludge combustion facilities is, in the current energy market, highly dependent upon extensive removal of water from sludge prior to incineration.

The extent of sludge volume reduction that can be achieved by processes for moisture removal is dramatic. For example, if the moisture content of a sludge is reduced from 99 percent (a common value for waste activated sludge) to 97 percent, sludge volume is reduced to essentially one-third of the initial value even though much water still remains in the sludge. As described in the following sections, removal of water is accomplished by thickening, dewatering, drying, and dehydrating processes, and the ease with which sludge releases water is improved by conditioning processes.

Thickening—

Thickening processes are those which accomplish significant removal of water while yielding a product that still flows as a liquid[c]. Thickeners usually produce significant reductions in sludge volume at comparatively low cost, and, thus, they are typical components of municipal sludge management schemes.

Thickening processes are of little consequence with regard to organic compounds in sludges. Organic compounds are predominately in the solid phase of municipal sludges, and their concentration is merely increased as a result of thickening. If long retention times are used (most likely, in gravity thickeners), then some solubilization of biodegradable organic compounds might occur during thickening, in which case some organic matter would be recycled back to the wastewater treatment plant with the liquid removed by thickening.

Thickening of municipal sludges is accomplished by use of gravity, centrifugal, or flotation thickeners. Gravity thickeners are simply sedimentation basins which afford the opportunity for suspended solids with a specific gravity greater than that of water to be concentrated at the bottom and clarified liquid to be removed from the top. Combined primary and secondary sludges from a municipal wastewater treatment plant at a concentration of, say, 3 percent solids by weight might thicken to a suspended solids concentration of about 6 percent solids by weight.

Although centrifuges[d] appear to be quite different than gravity thickeners, they, in fact, accomplish thickening by the same mechanisms that are involved in gravity thickening. Centrifugal force replaces the force of gravity as the cause of solids separation. Centrifuges are, thus, compact, intensive gravity thickeners. A centrifuge operated in the thickening mode at a municipal wastewater treatment plant might be expected to produce a thickened sludge concentration in the general order of 5 to 14 percent solids by weight.

Flotation thickeners also perform like gravity thickeners except that gravitational forces cause particles to move upward instead of downward because of the reduction in their specific gravity to a value less than that of the suspending medium--water. The specific gravity of the flocculent particles in municipal sludges normally is only slightly greater than that of water because of the large amount of water that they contain. By associating a gas (logically, air) with the light, flocculent, solids, their specific gravity can be readily reduced to the extent that flotation occurs. In most municipal sludge treatment applications, flotation is achieved by aerating water under pressure, reducing the pressure, and blending the supersaturated water with sludge to achieve reduction of the specific gravity of the solids. Flotation thickening has most commonly been applied to waste activated sludge. Typically, activated sludge enters a flotation thickener at around 1 percent solids by weight and is floated to a concentration of about 4 to 6 percent solids by weight (which is a much higher concentration than can be achieved by gravity thickening).

Dewatering—

Dewatering processes are used to achieve a higher degree of removal of water from sludges than is possible by thickening. The distinguishing characteristic of dewatering processes is that the product has a moisture content sufficiently low as to require handling by solids transporting techniques (for example, a conveyor belt) as opposed to the liquid transporting facilities (for example, pumping and piping) used to feed the sludge to the dewatering process. It should be recognized, however, that the water content of sludges fulfilling the definition of a dewatered sludge is still quite high. Municipal sludges containing 80 percent moisture typically display properties of a solid.

Dewatering of sludges is necessary prior to landfilling to reduce volume and achieve bearing capacity. It is also essential prior to combustion to limit fuel costs. Dewatering also may be justified to reduce transportation costs[c].

Like thickening, dewatering ordinarily does not affect the organic constituents of sludges other than by increasing their concentration because of removal of water. An exception is when sludge has previously been conditioned by heat treatment (see following section) in which case significant amounts of suspended organic material are solubilized and recycled back to the wastewater treatment plant.

Techniques used for dewatering municipal sludges vary from comparatively simple sand drying beds (on which liquid sludge is placed for gravity drainage and subsequent air drying) to complex mechanical dewatering devices such as vacuum filters, centrifuges[d], belt filter presses, and pressure filters.

Typically, sludge dewatered by mechanical techniques has a suspended solids content in the range from slightly less than 20 percent to somewhat more than 30 percent. Because of the large pressure differentials which can be used in pressure filtration, however, dewatered sludge suspended solids concentrations in the order of 50 percent often can be achieved (albeit at some sacrifice because of extensive conditioning requirements--see next section). Depending on the advantage which is taken of possibilities for air drying, sand bed dewatering facilities can be operated to yield dewatered sludge with a moisture content transcending the entire range of moisture contents achievable by mechanical sludge dewatering processes.

Conditioning—

The purpose of sludge conditioning processes is to alter the physical properties of sludges so as to improve dewatering characteristics. None of the mechanical dewatering processes mentioned in the previous section would ordinarily perform in an economically satisfactory matter without prior conditioning of sludge.

Mechanisms involved in sludge conditioning processes are poorly understood. Based on theoretical concepts of flow through porous media,[17] they must involve factors such as increased porosity and sludge particle size, and result in increased permeability and reduced compressibility of sludge. The precise mechanisms by which these alterations in the physical properties of sludges are achieved remain to be clarified, however, and assessment of conditioning requirements and effects must currently be carried out empirically.

Inorganic chemicals have traditionally been the most common means for chemical conditioning of sludges. In the United States, lime and ferric chloride have been the chemicals most often used. Additionally, organic conditioning agents (synthetic anionic, cationic, or nonionic organic polyelectrolytes) are common. Other means of sludge conditioning include thermal treatment, slow freezing and thawing, and use of admixtures such as fly ash.

Of the various conditioning techniques, heat treatment is of most concern with respect to organic compounds in sludge. This conditioning process involves exposure of sludge to "pressure cooker" conditions (approximately 200°C at about 200 psig for about 30 min). The improvement in sludge physical properties that occurs as a result of thermal conditioning is gained at the expense of appreciable solubilization of organic compounds. Garrison, et al[18], for example, indicated that 40 percent of the organic material contained in sludge as suspended solids was solubilized by heat treatment. Typically, heat treatment liquors contain 10,000 to 20,000 mg/L of chemical oxygen demand[19]. Effective heat treatment, thus, creates a substantial amount of organic material that requires treatment. Return of the heat treatment liquor to the wastewater treatment plant from which the sludge originated significantly increases oxygen requirements and sludge production. And further iterations result in more sludge production. Additionally, concern has been expressed about the effects of the nonbiodegradable organic constituents produced by heat treatment[20].

Drying and Dehydration—

Drying occurs following drainage on sand bed dewatering facilities and prior to burning in combustion facilities. Additionally, heat drying has been used as a separate process to achieve a high degree of moisture removal from solids. Such treatment is needed when it is necessary to give sludge a "shelf life" to allow marketing as an organic fertilizer. Separate heat drying is an energy intensive process and it is not common at municipal wastewater treatment plants[f].

In recent years, means for reducing drying costs by use of solvent extraction[21] or oil immersion[22] dehydration have been evaluated. Recently, an extensive study in the Los Angeles-Orange County Metropolitan Area[23] identified oil immersion dehydration as a potential process for future use in the Los Angeles metropolitan area.

Processes for Altering Sludge Quality

Some alteration of sludge properties may be necessary to make sludge suitable for ultimate disposal or reclamation. Processes such as sludge stabilization and combustion are comparatively common, established means for altering sludge properties. Other processes such as selective removal or destruction of toxic materials in sludges or inactivation of organisms and viruses are not currently common but are undergoing research and development.

Stabilization—

The purpose of sludge stabilization processes is to avoid nuisances that may accompany decomposition of organic material. Additionally, most stabilization processes accomplish significant reduction in the number of pathogenic organisms and viruses contained in the sludge.

The most common types of sludge stabilization processes involve biological degradation of organic materials under controlled aerobic or anaerobic conditions. Chemical stabilization processes have also been used. Chemical stabilization is achieved by creating conditions under which decomposition cannot occur. That is, chemical stabilization controls odor nuisances associated with decomposition of organic materials by preventing decomposition from taking place. In lime stabilization, the most common chemical sludge stabilization technique, decomposition of organic materials, is prevented by creating a pH high enough to slow the microbial breakdown of organics[24]. It should be emphasized that such high pH conditions should not be expected to prevail indefinitely in the environment; ultimately, the pH of lime stabilized sludge will fall and decomposition of organic materials will occur. Sludge chlorination is another chemical means of stabilization. In this case, the possibility for creating chlorinated organic compounds (and for solubilizing heavy metals and organic compounds[25]) may exist.

Biological stabilization of sludges has most frequently been accomplished using anaerobic processes. Anaerobic stabilization of sludges may simplistically be considered to involve two stages of microbial conversion of organic material. In the first stage, solubilization of complex organic solids occurs with production of carbon dioxide and simple organic compounds with comparatively low molecular weight. Then, obligately, anaerobic organisms convert the end product of the first stage into the final products, carbon dioxide and methane.

It might be noted that, whereas production of fuel from waste organic materials has become a popular topic in recent years, it has been common practice at municipal wastewater treatment plants throughout most of the century. Typically, anaerobic digester gas (which is about two-thirds methane) is used to maintain the temperature of anaerobic digesters at about 95° F, to fuel internal combustion engines, and/or to generate electricity. In the past, flaring of digester gas in excess of that needed for digester heat was common--especially at small municipal wastewater treatment facilities. Because of increasing energy costs, it is to be anticipated that flaring will become less common as the anaerobic digester gas is used to provide an increasing fraction of the total energy required for wastewater treatment[26].

Anaerobic stabilization commonly achieves about 50 percent reduction in the conventional organic solids contained in sludge. The product is a comparatively stable material which, while continuing to undergo biological change in the environment, does so at a rate that does not produce aesthetically objectionable conditions.

A wide variety of organic compounds can be biologically degraded under anaerobic conditions. To illustrate, Hovious, et al[27] found that all chromatographically identifiable organic compounds in petrochemical wastewater were destroyed under anaerobic conditions in a lagoon. Similarly, Healy and Young[28] reported that catechol and phenol were degraded anaerobically (following ring cleavage, products were stoichiometrically fermented to carbon dioxide and methane). Some organic compounds (notably, some of synthetic origin) are not degraded anaerobically, however, (or are degraded at very low rates). Iwata and Gunther[29] reported that DDT was metabolized in anaerobic digestion, but PCB remained intact. Numerous investigators, including Klein[30], have reported that NTA (nitrilotriacetic acid, an organic detergent builder) is not effectively degraded under anaerobic conditions[8]. Another synthetic organic detergent builder, CMSO (carboxymethyloxysuccinate), has been reported[31] to be anaerobically biodegradable following a period of acclimation.

Synthetic organic compounds in sludge dispatched to anaerobic digesters may also be of concern because of their toxicity to the organisms responsible for anaerobic stabilization. In this case, the digested product would contain not only the offending organic compound but, also, higher concentrations of ordinarily degradable organic compounds. Benson and Hunter[32], for example, found 0.4 mg/L of trichloroethane to be inhibitory to anaerobic digestion, and gas production halted temporarily at 1 mg/L. Comparable concentrations for trichlorotrifluoroethane were 4.8 and 20 mg/L. English investigators[33] have found anionic organic detergents in municipal sludges to inhibit anaerobic sludge stabilization.

Aerobic digestion is similar to anaerobic digestion in that it involves biological stabilization of degradable organic constituents suspended in liquid sludge. A major difference between the performance of the two processes is the higher oxidation-reduction potential of aerobically digested sludge (this is reflected in the presence of reduced compounds such as ammonium ions and hydrogen sulfide in anaerobically digested sludge as opposed to their oxidized counterparts, nitrate and sulfate ions, in aerobically stabilized sludges). Operationally, a major difference between the two processes is that anaerobic digestion produces energy, while aerobic stabilization (because of the need for supplying air or oxygen) consumes energy. One effect of the "energy crisis" has been to reduce the size of a wastewater treatment facility at which aerobic stabilization may prove advantageous because of operational convenience.

A third technique for biological stabilization of sludge is composting, which involves aerobic stabilization of dewatered sludge (or liquid sludge mixed with sufficient previously composted sludge or other agents to render it, effectively dewatered). A significant feature of sludge composting is its ability to achieve high temperatures (55° to 60°C for 5 days[34]) so as to inactivate microorganisms, viruses, and helminths contained in sludge[h]. Higgins, et al[35] reported that compost stabilization processes produce a higher degree of destruction of organic compounds than do competitive stabilization processes.

Composting of sludge is carried out by one of three basic means:

1. The windrow technique,
2. The static pile technique, and
3. Use of mechanical composting equipment.

These three composting processes differ only in the way that oxygen is supplied to the aerobic organisms responsible for sludge stabilization. In windrow composting, oxygen is supplied by periodic mechanical mixing of a long pile (a windrow). Static pile composting involves use of air compressors to pull air through elongated piles of dewatered sludge into perforated air headers located at the pile bottom (or to force air in the opposite direction). Mechanical composting involves use of a variety of different commercial equipment[36]--much of it developed in Europe--for assuring that oxygen is made available to composting sludge masses. A significant feature of the static pile composting method is that raw (previously unstabilized) sludges can be composted. Odors produced by turning of windrows preclude practical application of that technique to unstabilized sludge. The accommodation of unstabilized sludge in the pile technique of composting is achieved by discharge of gases removed from the compost pile through stacks of previously composted sludge where odor reduction occurs. An additional benefit of the pile composting method, if the pile is properly insulated with a blanket of previously composted sludge, is that all portions of the composting pile may reach the higher temperatures necessary for inactivation of organisms.

Combustion—

The combustion is the sludge treatment process that effects the greatest change in organic compounds--it destroys them. The principal end products of properly controlled combustion are carbon dioxide, water vapor, and inorganic ash. The high moisture content of sludge (even after dewatering) and the high organic content of sludge solids, results in appreciable volume reduction; however, ash and exhaust scrubber water still remain.

The potential air pollutants in municipal sludge incinerator exhaust include particulates, sulfur and nitrogen oxides, carbon monoxide, heavy metals, heat, and organic compounds. On the basis of limited available data[i], the pollutants of greatest potential concern in the discharge from properly designed and operated incinerators equipped with scrubbers would seem to be lead, cadmium, and organic compounds.

Thermal decomposition is, of course, a common means for destroying concentrated hazardous organic wastes; however, temperatures prescribed for such operations are higher than those usually achieved in municipal sludge incinerators. Nevertheless, the limited information available suggests that appreciable removal of organic priority pollutants occurs at the lower temperatures prevailing in municipal sludge incinerators. For example, an EPA Sewage Sludge Incineration Task Force[37] monitored five different pesticides and PCB's in operating municipal fluidized bed and multiple hearth furnaces and reported that the pesticides and PCB's could not be detected in ash or scrubber water. The TaskForce inferred that the compounds were destroyed in the furnace and were absent in the furnace exhaust. In other studies[38], the fate of PCB's and pesticides added to sludges was monitored; 99 percent of the pesticides and 94 percent of the PCB's were destroyed.

In the United States, sludge combustion using an excess of oxygen (from air) in multiple hearth or fluidized bed furnaces is most common. Possible advantages of starved air combustion (pyrolysis) have been investigated. Although pyrolysis of municipal sludges has been demonstrated at full scale[39], the process is not in continuous full scale use. Another combustion variation is wet air oxidation, in which high pressure is used to allow combustion of organic compounds while sludge remains in liquid form[j]. The largest municipal installation of its kind, in Chicago, has been taken out of service--presumably because of maintenance problems.

The two most common types of municipal sludge combustion equipment (multiple hearth furnaces and fluidized bed furnaces) affect organic compounds differently: gases leaving a fluidized bed furnace are hotter than those leaving a multiple hearth furnace. Because of the countercurrent flow of sludge and combustion gases in multiple hearth furnaces, the sludge remains "cool" until its appreciable water content is evaporated. The evaporation cools the exhaust gas, increasing the possibility that organic compounds are volatilized and removed from the furnace unburned. Such organic compounds could be odor-causing substances, photochemical reactants, or toxic materials. Afterburners can be used to control organic emissions from multiple hearth furnaces, but at an appreciable cost for fuel. Zang[40] has argued that the operation of municipal multiple hearth sludge incinerators can be controlled to eliminate the need for afterburners; and 95 percent destruction of PCB's has been achieved in a multiple hearth furnace with no afterburning[41].

Facilities for sludge combustion are intimately associated with the conditioning and dewatering processes considered in a previous section. A major cost for energy in sludge combustion results from evaporation of the large amounts of water associated with sludge solids. This cost can be reduced by effective dewatering prior to combustion; however, achieving a high degree of dewatering is also expensive.

In recent years, production of energy through combustion of organic compounds in municipal sludge has frequently been suggested; however, sludge combustion facilities usually consume energy[k]. Future advancements in sludge combustion might include improved combustion and heat recovery technology and improved capability for conditioning and dewatering sludges.

Inactivation of Organisms and Viruses—

Inactivation of microorganisms, helminths, and viruses occurs incidentally in some processes for sludge treatment. Sludge incineration is one obvious example. Inactivation of organisms and viruses also occurs in thermal conditioning and certain stabilization and chemical conditioning processes. Biological stabilization processes operated at mesophilic temperatures can achieve appreciable reduction in the number of pathogenic organisms and viruses, but not their elimination. A high degree of destruction of organisms and viruses may be achieved by use of thermophilic biological stabilization processes (composting or thermophilic aerobic or anaerobic digestion).

The use of special processes to inactivate organisms and viruses in sludge prior to sludge application on land has been suggested in recent years. Whereas anaerobic digestion (the process most commonly used prior to land application) causes a dramatic reduction in the population of pathogenic helminths, microorganisms, and viruses, they may still be present in substantial numbers in sludge being applied to land[42]. Epidemiological evidence justifying the need for destruction of organisms in anaerobically digested sludge prior to land application has not been developed, however[1].

The inactivation processes of principal interest are heat pasteurization, and radiation using isotopes or high energy electrons. All three of these processes have been demonstrated at comparatively large scale[m] but none is in common use.

Use of high-energy electrons for inactivation of organisms in sludges may be of interest from the standpoint of control of organic materials in sludges because of the possible concurrent alteration of organic molecules resistant to biological degradation. Similarly, the possibility of using gamma radiation to degrade persistent organic compounds in waste has been suggested (for example, see Cappadona, et al.[43] and Vollner, et al.[44]). Trump, et al.[45] has demonstrated that PCB's in water are destroyed using high energy electron dosages far less than those which would be used to inactivate organisms. However, because such compounds become associated with organic material such as lipids, their inactivation in municipal sludges may not be so readily achieved.

Detoxification Processes—

Detoxification processes remove potentially offensive constituents from sludges. Because detoxification technology is emerging, it is difficult to cite examples of current applications in municipal sludge management practice. The extent of future development and implementation of detoxification processes will depend upon: (1) the degree to which source control and pretreatment serve to modify the quality of sludges from municipal wastewater treatment, and (2) the stringency of sludge quality standards necessary to protect environmental quality and human health.

Removal of heavy metals and destruction of toxic organic compounds are the best illustrations of detoxification processes applicable to municipal sludges. Attempts at heavy metal removal ordinarily take the form of acidification (to solubilize heavy metals and permit their extraction by removal of moisture from sludge). The extraction process can be reasonably effective[46], but it leaves behind a low pH wastewater containing an assortment of heavy metals.

Work on destruction of toxic organic compounds in municipal wastewater residues has been limited principally to the preliminary work on high energy electron radiation and radioisotope radiation described in the previous section (and, of course, sludge combustion is used).

In view of the relatively dilute concentrations of toxic metals and organic compounds in municipal sludges, detoxification will be expensive (certainly costs per unit of toxic material removed will be high). It is to be hoped that effective source control and pretreatment practices will minimize the necessity for implementing such processes.

ULTIMATE RECLAMATION OR DISPOSAL OF MUNICIPAL SLUDGES

After treatment, municipal wastewater sludges must either be recycled into productive use or disposed of as waste materials. The options available for ultimate reuse or disposal are extremely limited. Reclamation opportunities are scarce, and disposal is possible only to air, water, and land. Opportunities for environmentally acceptable disposal of sludge constituents to air are limited (combustion and biological stabilization result in some disposal to air, but either of these processes leaves residues requiring reuse or disposal). Practicable options, thus, are limited to sludge reclamation or sludge disposal to water or land. These possibilities are considered in this section.

Reclamation of Sludge Constituents

Municipal sludges are constituted from a remarkably heterogeneous collection of substances--each contained in comparatively dilute concentration and frustratingly difficult to separate from the others. To date, this inherent characteristic has prevented widespread use of reclamation schemes. The only common sludge reuse scheme which can be cited--application of sludge to agricultural land--makes use of sludge in heterogeneous form. This practice is considered in a later section on land application. Some additional, but largely unrealized, possibilities for reclamation are reviewed here.

The potential attractiveness of reclamation of sludge constituents is illustrated by Hurwitz's[6] estimate that the amino acids in municipal sludge are worth $12,000 to $25,000 per ton of dry solids (in 1957 dollars). However, the appreciable reward for amino acid extraction (as well as for extraction of other constituents such as vitamins and precious metals) awaits development of practicable technology.

Extraction of protein from waste-activated sludge has been considered[47], but not carried out at full scale. Use of activated sludge as a component in the diet of a wide variety of animals has been practiced by certain industries[48] which can control sludge quality, but use of waste-activated sludge as an animal food supplement is not common in municipal waste management practice.

Development of construction materials, production of activated carbon[49], extraction of metals[46], and recovery of wastewater treatment chemicals[50] have been considered and, in some instances, carried out. However, as a practical matter, none of these reclamation practices are in common use.

Ultimate Disposal to Water

Disposal of sludge to fresh water is not a viable option. However, the vastness of oceans has led to their use in assimilation of wastewater treatment residues. Ocean discharge of sludge, as currently practiced, is strictly a disposal technique--ocean disposal systems are not being designed to make productive use of sludge constituents in mariculture projects.

It was generally considered that ocean dumping of sludges in the United States was barred after December 31, 1981[n] by a 1977 amendment[51] to the Marine Protection, Research and Sanctuaries Act. Recently, however, a Federal District Court judge ruled that statutory conditions in the Marine Protection, Research and Sanctuaries Act must be considered in determining whether ocean dumping of sewage sludge unreasonably degrades the marine environment[52]. Regardless of the ultimate status of ocean discharge of sludge, the legislation had a major impact on coastal cities because of the economic attractiveness of ocean dumping, and the difficulty in identifying environmentally suitable land-based sludge disposal alternatives that would be accepted by the public. Indeed, much of the municipal sludge management activity during the 1970's represented efforts by coastal cities to identify suitable land-based alternatives (and to influence federal ocean dumping policy). The reader is referred to reports of activities at Philadelphia[53,54], New York City[55,56], and Los Angeles[23,57] for a perspective on the complexity of management of residues from large metropolitan areas when a major change in disposal practices is required[o].

Some of the potentially adverse effects of ocean discharge of municipal sludge include toxicity and food chain impacts from heavy metals, unwanted coastal water enrichment from nutrients, disease transmission from pathogenic organisms and viruses, oxygen depletion from biodegradable organics, and toxicity and food chain impacts from recalcitrant organic compounds. In accordance with the focus of this Monograph, the last two possible effects are considered briefly here.

Control of oxygen depletion in ocean waters due to the presence of biodegradable organic materials in municipal sludges is not a substantial technical challenge[p]. Traditionally, municipal sludges have been biologically stabilized prior to ocean discharge so that their oxygen-demanding capability is diminished. Dispersal serves as an additional means to avoid high local demand for oxygen.

As with other techniques for sludge utilization and disposal, organic priority pollutants in sludge may present a more formidable challenge. Control of such organic compounds at their source would represent the preferred solution. The degree of structuring of marine food webs was studied by Young and Mearns[58] so as to anticipate the extent of food chain biomagnification. Heavy metal biomagnification did not occur because of absence of adequate structure in the food chain, but the sum of DDT and a PCB did increase with trophic level--presumably because of the long biological half-life of these constituents. Similar results have been reported by Bascom[59].

In addition to long-term food chain effects, organic priority pollutants also may produce effects in marine environments of more immediate nature. Fin erosion in bottom-dwelling fish has been reported in areas of waste discharge off both the Atlantic and Pacific coasts of the United States as well as elsewhere in the world. It has been hypothesized[60,61] that exposure to PCB's in bottom sediments may be a factor in development of fin rot[q]. Another possibility for short-term effects arises from the influence of toxic organic substances on aquatic food chains. O'Connor, et al[62], for example, suggested that PCB's reduced the size of marine phytoplankton and, thus, might affect the amount of harvestable fish.

Ultimate Disposal to the Land

As a practical matter, the most residues produced by wastewater treatment currently must be placed on land. This is necessitated by the absence of suitable technology for recycling sludge constituents, and by controls on the disposal of wastewater treatment residues elsewhere in the environment.

Strategies in placing sludge on land involve either concentration or dispersal of residues. If the concentration strategy is used, the result is some form of lagoon or landfill. The dispersal strategy involves use of liquid, dewatered, or dried sludge in agriculture or silviculture, application to park land, use in rehabilitation of spoils or low quality land, and similar practices in which sludge is widely distributed on land.

Even though most attention is given to application of sludge on agricultural land, more municipal wastewater treatment residues currently end up in lagoons or landfills. Farrell[63] estimated that 40 percent of municipal sludge was being placed in landfills in 1972 and that the fraction would remain the same in 1985. Beneficial utilization on land was estimated to account for 20 percent of municipal sludge in 1972 and 25 percent in 1985. (Corresponding 1972 and 1985 estimates for incineration were 25 percent and 35 percent while ocean discharge was estimated at 15 percent and 0 percent, respectively.)

Landfills for municipal wastewater treatment sludge vary widely. The nature of preceding wastewater and sludge treatment, the extent of inclusion of other waste materials, climatic conditions, and soil and hydrogeological characteristics, all can vary widely from one sludge landfill to another. Common characteristics of municipal sludge landfills are that: (1) decomposition of biodegradable organic compounds occurs (ordinarily under anaerobic conditions with the production of methane gas which may be collected more commonly in the future), (2) depending on local conditions, production of a leachate containing high concentrations of organic compounds may occur, and (3) they fill in time. Readers are referred to the U.S. EPA

Process Design Manual on Municipal Sludge Landfills[64] for details on variations in municipal sludge landfill practices.

Recent interest has focused on municipal solid-waste landfills and industrial hazardous-waste landfills. Little attention has been given to purely municipal sludge landfills (which generally differ only in degree from the other two types). Design and operational aspects such as gas generation and capture, leachate production and treatment, and avoidance of groundwater contamination and similar. Readers are referred to Chapter 14 of this Monograph for additional information.

The past decade produced dramatic changes in practices concerning application of municipal wastewater sludges to agricultural land. Use of sludge on agricultural land was commonplace at both the beginning and end of the 1970's, but the philosophy guiding application practices changed. At the beginning of the decade, the focus was on sludge disposal with a tacit goal of maximizing the areal rate of sludge application. By the end of the decade, the focus had shifted to environmental quality control and health protection with a goal of restricting sludge application rates to levels necessary to control water, land, and crop quality[5].

The beneficial effects of application of controlled amounts of "clean" municipal wastewater sludge to agricultural land are generally not debated. However, differences in views are pronounced regarding the potential detrimental effects of municipal sludge application of land. The principal potential detrimental effects are:

1. Disease transmission by pathogenic organisms.
2. Plant toxicity due to phosphorus.
3. Infant methemoglobinemia (particularly via ground water) or surface water enrichment due to nitrogen compounds.
4. Phytotoxicity due to salts.
5. Phytotoxicity or food chain effects of heavy metals.
6. Toxicity to soil organisms and food chain effects of persistent organic materials.

In this chapter, these potential detrimental effects are considered only in the context of organic compounds in sludge. For more comprehensive discussion, readers are referred to documents such as the EPA Technical Bulletin[65], a bulletin prepared by committees of the North Central and Western State Agricultural Experiment Stations[66], and the appraisal of heavy metal hazards by the Council for Agricultural Science and Technology[67].

The high concentrations of "ordinary" organic compounds contained in municipal wastewater sludges (even after biological stabilization processes) significantly affect soil properties and the fate of other sludge constituents in the soil. Organic compounds in soil can play major roles in preventing plant uptake and migration of heavy metals because of factors such as low solubility of metal complex species, adsorption of the metal complexes on soil, and reduced coulombic repulsion[68]. Some organic compounds, on the other hand, can serve to mobilize heavy metals because of formation of soluble complexes. The synthetic organic detergent builder, NTA, is an example[68,69]. Furthermore, biodegradation of organic compounds that inhibit heavy metal adsorption might be slowed when they are associated with heavy metals[70].

"Ordinary" organic compounds from sludge applied to soil might also influence the fate of synthetic organic chemicals in the same sludge. Terry, et al.[71] have reported that the rapid decomposition of sludge organics following sludge application to land exerts a "priming" effect which hastens the rate of degradation of other organics in the soil. Indeed, Ward, et al.[72] and others have considered the possibility of detoxifying herbicide wastes by applying them to soil enriched with sewage sludge[5]. Cometabolism of synthetic organic compounds has been discussed in detail by Alexander[73].

In addition to adsorption and microbial degradation, the fate of synthetic organic substances added to soil in sludge may be affected by photodecomposition, chemical reactions, volatilization, plant uptake, leachate and runoff[74]. The relative significance of these various mechanisms depends on the nature of the synthetic organic compounds, soil type, soil organic content, soil moisture, temperature, nutrient availability, and other factors. The combined influence of the various mechanisms is reflected in data such as those presented by Nash and Harris[75] on the persistence of nine different chlorinated hydrocarbon insecticides in soils. After 16 years, they found that 7 to 49 percent of the original amounts was still present.

Data on the persistence of synthetic organic compounds other than insecticides, pesticides, and herbicides are limited. Polybrominated biphenyl (PBB--the contaminant in Michigan animal feed[76] has been found to have low biodegradability, low volatility, low solubility, low plant uptake, and therefore, is a "rather permanent component of contaminated soils"[77]. PCB's have been found to resist leaching by water, and their volatility is reduced by adsorption to soil and soil organics[78]. Slightly chlorinated PCB's are more readily biodegraded than highly chlorinated PCB's, and nearly all PCB's apparently taken up by carrots were associated with the peel[29]. In an incident where high concentrations of PCB's were contained in municipal sewage sludge applied to soil[79], PCB's were detected in cow's milk (at 5 ppm) and in vegetables. The detergent builder, NTA, was nearly completely degraded in aerobic soil but not at all in anaerobic soil[80], while another builder, CMOS (carboxymethyloxysuccinate), was degraded in aerobic soils following acclimation[81].

Very little information is available about the possible long-term health risks associated with those synthetic organic compounds that do persist in soils. Majeti and Clark[82] recently called for more research on crop uptake of organic chemicals and on pertinent chronic human health effects.

FUTURE DEVELOPMENTS IN MUNICIPAL SLUDGE MANAGEMENT

Traditionally, sludge management has received a disproportionately small share of the attention of those concerned with the development of technology for waste management. There is, therefore, a corresponding need for research and development to improve current capabilities to effectively manage wastewater residues, to reduce the costs of residue management, and to control the environmental effects of residues. Particular attention is given here to desirable developments that concern organic compounds in sludges. First, however, a few of the major needs associated with other aspects of sludge management are reviewed.

Desirable Overall Municipal Sludge Management Developments

Present municipal sludge management practices evolved primarily on an empirical basis. Basic understanding of sludge management has lagged behind the actual development of sludge management techniques. Elaboration of the fundamental factors that control the physical, chemical, and biological properties of sludges, the fundamental mechanisms that determine the performance of sludge management processes, and the fundamental concepts that establish the environmental effects of sludge management practices remains, for the most part, to be completed.

Improved understanding of the basic chemical, physical, and biological properties of sludge is essential for future improvements in sludge management capabilities. Such understanding could lead to source control and pretreatment practices and to wastewater treatment systems that would yield sludges with properties most suitable for economical and environmentally acceptable treatment, utilization, and disposal procedures.

Major reduction in the cost of municipal sludge management might be achieved by improved understanding of the physical properties of sludges, the factors that influence these properties, and the ways by which they can be altered. The need for these improvements may be appreciated by considering that, at present, some municipal sludges from biological wastewater treatment cannot be concentrated by gravity sedimentation to a suspended solids concentration as high as one percent by weight. Dewatering of such sludges is exceedingly difficult and expensive. Yet, removal of moisture is essential prior to combustion, landfilling, and composting and can significantly reduce the cost of other processes such as digestion, transportation, and storage.

An improved understanding of the chemical properties of sludges is needed to permit effective control of chemical constituents of concern and to provide a basis for controlled alteration of the physical properties of sludges. Similarly, improved understanding of the biological characteristics of sludges could provide a basis for controlling and enhancing chemical and physical properties. For example, development of capability to optimally regulate bioflocculation could significantly reduce current sludge management costs, and improved ability to control the microbial uptake, utilization, or release of wastewater and sludge constituents could extend current sludge management capabilities.

There is need to move from the current empirical approaches for designing and operating sludge treatment processes to approaches that derive from basic understanding of the fundamental mechanisms involved. This requires further knowledge of the influence of the physical, chemical, and biological properties of sludges on the performance of each of the various sludge treatment processes. The efforts to regulate sludge properties described in previous paragraphs should be linked to advancements in treatment process design to achieve economical and effective processing. An important by-product of such research could be fundamental insights that lead to sludge management processes that are unimagined currently.

On the basis of resource, energy, and environmental considerations, it seems inevitable that present emphasis on sludge "disposal" must, in the future, be replaced by emphasis on sludge "reclamation." Ideally, the advances in basic understanding of sludge properties and treatment processes considered in previous paragraphs would, in time, lead to an ability to economically sort sludges into their basic constituents for recycle into the productive cycles. Practically, even something short of this goal would be a vast improvement over current practices.

Capabilities for returning unreclaimed sludge constituents to the environment must be improved. This requires a much more rigorous understanding of the fate and effects of sludge constituents in soils and in oceans. These advances, too, must be tied to work on basic properties of sludges and basic performance of treatment processes in order to achieve overall integrated waste management schemes that are effective and economical.

Sludge management inevitably involves risks. Abilities to monitor and assess risks of alternative approaches need to be improved. This should come, in part, from the advances in basic understanding advocated earlier.

Sludge management also inevitably involves people. As in the past, implementation of future developments in municipal sludge management will be influenced by perceptions of the public. Improved ability to control, predict, and monitor the performance of sludge management schemes should aid in achieving public acceptance, but it would seem that more attention also is due in the future to the social aspects of residue management.

Desirable Future Developments Concerning Organic Compounds in Sludge

A major step in controlling the environmental impact of organic compounds in municipal wastewater treatment residues is to control the quality of the wastewater from which the residues originate. Source control and pretreatment of industrial discharges is a necessary, but, probably, inadequate means of sludge quality control. Modification of product formulations and, even, life styles may, in the long-term, be warranted.

Improved understanding is needed of the mechanisms that control incorporation of organic compounds into the various residues produced at municipal wastewater treatment facilities. Such knowledge could lead to ability to control the concentration of organic compounds in various residues. Perhaps, for example, most synthetic organic compounds could be caused to accumulate in a single residue--possibly skimmings. Alternatively, improved understanding of basic removal mechanisms might lead to development of new wastewater treatment practices to effect selective removal of organic compounds of concern.

Improved understanding is needed of the mechanisms of biodegradation of synthetic organic compounds in wastewater treatment processes, in sludge management processes, and in the environment. Process modifications needed to maximize degradation could then be implemented, and economical means for altering organic compounds to achieve biodegradation could be sought.

The fate of synthetic organic compounds in each sludge management process needs to be determined and related to fundamental causative mechanisms. Because the fate of organics in many sludge treatment processes is established by their distribution between the liquid and solid phases of sludge, more information is needed on the nature of the association of specific organic molecules with the solid phase of sludge and the influence of various processing techniques on that association. Loss of organics to the gaseous phase (perhaps during vacuum filtration) also must be explored.

Based on fundamental knowledge of the fate of organic compounds in sludge treatment processes, opportunities for removing or destroying them can be sought. Given the ubiquitous distribution of some recalcitrant organics and their tendency to concentrate in wastewater sludges, effective sludge treatment might represent an opportunity to extract some organic compounds from the environment.

The possible role of organic compounds in influencing the removal or behavior of other sludge constituents must be determined. Mobilization of metals through formation of soluble complexes and interference with biological degradation of ordinary organic compounds are examples.

The fate and effects of organic compounds in sludges in reclamation and disposal schemes must be more clearly established. Mechanisms that control the destruction and transport of organic compounds in soils and oceans must be understood so that discharge to the environment can be accomplished in a fashion that minimizes risk. Similarly, biological uptake of organic compounds from sludge and food chain implications in terrestrial and marine environments must be understood more completely so as to minimize their adverse environmental and health effects.

NOTES

a. Some have noted that sulfur-containing amino acids are deficient--a problem common to single cell protein production also.

b. Some emphasize the low nutrient content of municipal sludges. They use commercial inorganic fertilizers as their basis for comparison. In making beneficial use of sludge nutrients in agriculture, sufficient sludge can be applied to achieve the desired amount of nitrogen or phosphorus. Limitations on areal rates of application of nutrients, in fact, ordinarily limit the amount of sludge that can be applied to land.

c. Even at very dilute concentrations[83], sludges display complex flow behavior. Because of the existence of a solid phase, sludges behave as pseudoplastic or plastic materials[84]. Additionally, sludges usually are thixotropic[85]--that is, their flow properties change with time. These characteristics of sludges lead to complexities in design of pumping and piping installations as well as in effective design and operation of other facilities whose performance depends on the rheological properties of sludges.

d. Note that centrifuges can be used as either thickening or dewatering devices. In the former case, they produce a product displaying fluid-like properties, while in the latter, the product must be moved by solids-handling techniques.

e. Note, however, that dewatering of sludge is expensive. Significant transportation distances ordinarily are required to justify dewatering solely on the basis of transportation cost reduction. Illustrative calculations by the author[86], for example, indicate that dewatering is not economically justified in municipal sludge management schemes involving less than 20 mile transport to agricultural land disposal sites regardless of the size of the wastewater treatment facility.

f. Indeed, the Metropolitan Sanitary District of Greater Chicago recently has announced its intention of closing down heat drying facilities.

g. In contrast, Moore and Barth[87] did obtain NTA degradation under anaerobic conditions. Biodegradation occurred only when the digester received aerobic biological sludge that was acclimated to NTA.

h. It should be noted, however, that maintenance of thermophilic temperatures without energy addition also is possible in anaerobic and aerobic digestion processes. In anaerobic digestion, thermophilic temperatures are achieved by burning methane gas produced in the course of digestion. The process is rare in the United States (although it has been demonstrated at full scale[88]) but comparatively common in the Soviet Union[89]. Thermophilic conditions in aerobic digestion processes can be achieved by use of pure oxygen[90] to reduce the loss of heat associated with the large volumes of nitrogen involved when air is used as the oxygen source or, as demonstrated recently by Jewell and Kabrick[91], by use of a self-aspirating mechanical aerator that avoids excessive heat loss.

i. Information on municipal sludge incineration emissions has been summarized by Farrell and Salotto[37], Shen[92] and Helfand[93].

j. Wet air oxidation of sludge involves the same type of equipment as is used in some thermal conditioning processes. A continuum of temperature and pressure conditions exists with higher degrees of oxidation of organic compounds occurring as temperature and pressure are increased. Like thermal conditioning, wet air oxidation produces a liquid phase with high concentrations of dissolved organic materials[94].

k. Note that accounting practices for determining energy balances in sludge combustion processes are not highly developed. Reports of self-sustaining sludge combustion often exclude related primary or secondary energy consumption. An example of a related, but usually excluded, energy requirement is the increased energy needed to supply oxygen in biological treatment processes that receive recycled liquid containing high concentrations of organic compounds from thermal conditioning processes used to achieve highly dewatered sludge prior to combustion. Another illustration is the coincineration of sludge and municipal refuse. Self-sustaining combustion is readily achieved by coincineration, but inclusion of sludge reduces net power production from refuse combustion or decreases the amount of available RDF (refuse derived fuel).

l. As noted by Love, et al.[95] epidemiologic data on enteric diseases are notoriously poor, however. For reviews of the potential significance of sludge in disease transmission, see Hays[96] and Love, et al.[95].

m. Developments related to sludge pasteurization were reviewed by Stern[97]. Use of high energy electron radiation at a 380 m^3/day facility at the Boston Deer Island Wastewater Treatment Plant was described by Trump, et al.[98]. Experiences at the Abwasserverband Ampergruppe in Geiselbullach in the Federal Republic of Germany with a 30 m^3/day facility for sludge radiation using ^{60}Co were reviewed by Lessel, et al.[99]. Brandon[100] summarized related work at Sandia Laboratories as a part of research on beneficial use of radioisotopes from nuclear reactor wastes.

n. Ocean dumping was, effectively, previously banned by the criteria for issuing ocean dumping permits developed under provisions of 1972 Marine Protection, Research, and Sanctuaries Act and the Federal Water Pollution Control Act. Thus, planning to develop land-based alternatives to ocean dumping was underway before the 1977 legislation was inacted.

o. The banning of ocean discharge of municipal wastewater sludge has been--and continues to be--a controversial environmental issue. Thus, the General Accounting Office[101] noted that proposed alternatives to ocean disposal may be more environmentally harmful, two committees of the National Academy of Sciences[3,102] advised against protection of one segment of the environment without consideration of impacts on other segments, and, on the basis of studies of the effect of sludge management, the Commission on the Coastal Water Research Project[103] considered that the public opinion on the ocean "has been mislead by the press, television, and 'documentary' motion pictures."

p. Bascom[104], quoting Isaacs, noted that a single marine species, anchovies, off the southern California coast produces ten times as much fecal matter daily as does the population of Los Angeles.

q. Indeed, Sherwood[61] has suggested the use of fin erosion in bottom-dwelling fish as an environmental indicator.

r. The 1970's also brought new terminology, with lands receiving sludge according to the former philosophy now being termed "dedicated" lands.

s. On the other hand, soil organics may reduce the biodegradability of adsorbed persistent organic compounds[105].

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REDUCTION OF ORGANICS BY BIOLOGICAL TREATMENT

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INTRODUCTION

General

Biological waste treatment processes utilize microorganisms to remove organic substances from wastewaters and thereby minimize pollution of the nation's water resource and help meet the nation's water quality objectives.

The majority of biological processes used to produce a well treated effluent are aerobic in nature. Examples include activated sludge units, trickling filters, aerated lagoons, oxidation ditches, and rotating biological contacting units. This chapter describes only the major aerobic processes, the factors affecting removal of organics, and typical process performance.

Anaerobic biological treatment processes are not discussed. While such processes can be a component of a waste treatment system, they rarely are used as the major biological process to produce an effluent suitable for direct discharge to surface waters.

The intent of this chapter is to identify the type and quantity of organics that can be removed from untreated industrial as well as municipal wastewater by typical aerobic biological treatment processes. The chapter is not intended to be a detailed guide to design and operation of biological wastewater treatment systems, but rather, to provide the general scientist a basis for improved understanding of the processes most commonly used in treating wastewaters.

Treatment Systems

Biological treatment processes normally are one component of a total treatment system (Fig. 1). Preliminary and primary treatment processes remove the large and settleable solids while biological treatment processes remove soluble compounds and solids not removed in the primary processes. A secondary clarification unit generally is part of the biological treatment process. The secondary clarification unit removes the microorganisms discharged from the biological processes before the treated effluent is discharged either directly to receiving waters or to additional treatment processes. With many biological treatment processes, part of the microbial

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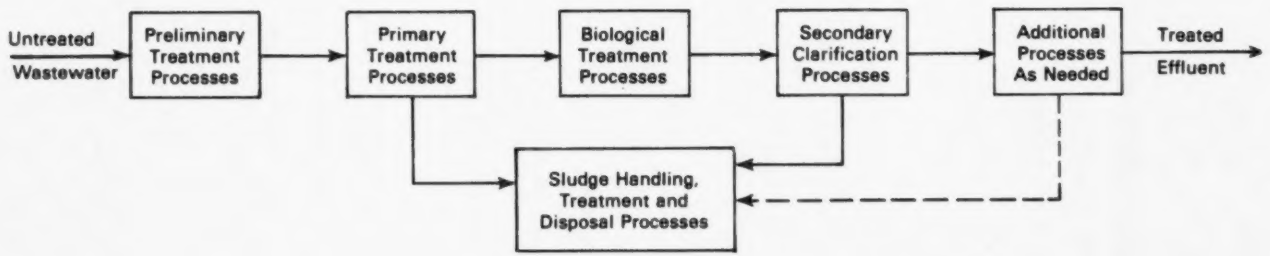
Untreated
Wastewater
Preliminary Treatment Processes
Primary Treatment Processes
Biological Treatment Processes
Secondary Clarification Processes
Additional Processes As Needed
Treated
Effluent
Sludge Handling, Treatment and Disposal Processes

Figure 1. Typical components of a wastewater treatment system.

solids removed in the secondary clarification processes are returned to the biological unit to enhance its performance.

Depending upon the degree of treatment needed, additional processes such as chlorination to reduce the bacterial concentration, filters to reduce the suspended solids concentration, activated carbon to adsorb soluble organics, and chemical precipitation to remove phosphorus may be needed after biological treatment. The primary treatment processes, the biological treatment processes, and some of the additional processes produce solids, known as sludge, that must be handled, treated and processed prior to disposal.

Treatment systems are designed and operated to achieve certain goals: either specific effluent limitations or water quality criteria (Fig. 2). The effluent limitations represent those limits felt to be practically and economically achievable by available treatment technology. Water quality criteria are established to safeguard uses of the receiving water, such as public water supply, recreation, or irrigation. These goals are established by federal and state agencies.

Legislation

The objectives of wastewater treatment that are to be achieved by municipalities and industries have been established by federal legislation. The Federal Water Pollution Control Act Amendments of 1972 required industrial dischargers to meet effluent limitations that can be achieved by the application of the best practicable control technology currently available (BPT) and the best available technology economically achievable (BAT). Pretreatment standards were to be developed for industrial wastes discharged to publicly owned treatment works (POTW). The Act also imposed an obligation on the Environmental Protection Agency (EPA) to promulgate regulations restricting the discharge of toxic chemicals.

EPA was unable to meet all of the deadlines set by the Act and was sued by environmental groups. The settlement agreement of the lawsuit required EPA to develop a program for promulgating BAT effluent limitations guidelines, pretreatment standards, and new source performance standards for 65 "priority" pollutants and classes of pollutants. The 65 classes were expanded to a list of 129 specific pollutants. These can be grouped into ten categories (Table 1).

The Clean Water Act of 1977 (CWA) incorporated the basic elements of the settlement agreement for toxic pollutant control. As a result, pollutants were grouped into three broad categories:

- *conventional* — biochemical oxygen demand (BOD), total suspended solids (TSS), fecal coliform bacteria, pH, and oil and grease (O&G)
- *toxic* — the priority pollutants and others that may be so identified by EPA
- *nonconventional* — all others which are not specifically listed as either toxic or conventional; examples include color, chlorides, total dissolved solids, and turbidity.

The effluent limitations guidelines and standards that EPA identifies for each industry are technology-based. Treatment processes that are capable of controlling the pollutants from an industry are identified and the long-term performance, operational limitations and reliability of each process are assessed. The costs associated with such control methods also are evaluated. After consideration of these and other factors, specific control and treatment technologies are identified as applicable to an industry and effluent limitations and standards are specified for each industrial subcategory. The regulations do not require the installation of a particular technology. It is the responsibility of each industry to use or develop technology that can economically achieve the effluent limitations.

Where technically and economically possible, effluent limitations can reflect the complete control of wastewaters and thereby achieve the ultimate goal of

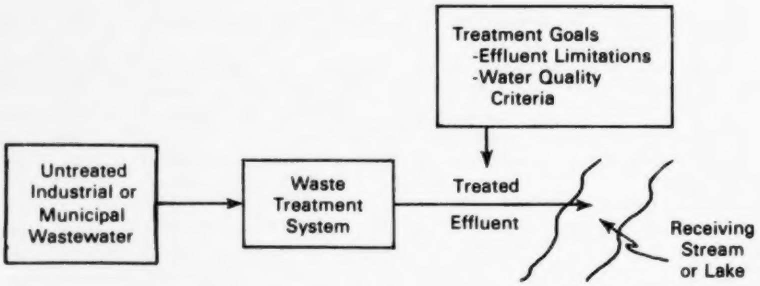

Figure 2. A waste treatment system is designed and operated to achieve specific goals.

"no-discharge" of pollutants from an industry. This can be accomplished by recycle and reuse, by "dry" waste cleanup procedures, or by controlled land treatment of the wastewaters.

Thus, there is an emphasis on the control of conventional, nonconventional, and toxic organic pollutants in industrial wastewaters. Efforts are underway to quantify the removal of all types of organics, especially the organic priority pollutants, in various treatment processes and systems.

ORGANIC POLLUTANTS

General

There are many organic compounds in wastewater and many methods are used to identify and quantify them, and to remove them. Organic compounds are composed of carbon in combination with one or more elements, generally hydrogen and oxygen. Other elements commonly found in naturally occurring organic compounds are nitrogen, phosphorus, sulfur, and iron. The principal natural organic compounds found in wastewater are proteins, carbohydrates and fats and oils (also known as oils and greases). Synthetic organic compounds containing halogens, metals and many other elements also can be found in wastewaters. Generally, nonspecific methods are used to measure these organic compounds in wastewaters (Table 2).

Biodegradable Organics

The most widely used parameter to measure organic matter in wastewater is the five-day biochemical oxygen demand (BOD_5). BOD is the amount of oxygen required by bacteria while decomposing organic matter under aerobic conditions.

The BOD test is a bioassay which measures the oxygen consumed by living organisms as they metabolize the organic matter in a waste. The test is conducted under conditions as similar as possible to those that may occur in nature. Theoretically, infinite time is required for complete oxidation of the organic matter. Normally, a large fraction of the oxidation takes place in five days. Standard conditions of 20°C incubation and 5 days are used to assure consistent and reproducible results.

The BOD test is the only available test that provides a reasonable measure of the impact that untreated and treated wastewaters will have on the dissolved oxygen resources of surface waters. The microorganisms used in the test are the link between

Table 1. Categories of the Priority Pollutants[1]

Pollutant	Remarks
Pesticides	Generally chlorinated hydrocarbons — concentrated through the food chain
Polychlorinated biphenyls (PCBs)	Used in electrical capacitors and transformers, paints, plastics, insecticides, other industrial products — fat soluble, subject to biomagnification
Metals and other inorganics	Antimony, arsenic, beryllium, cadmium, copper, lead, mercury, nickel, selenium, silver, thallium, zinc, asbestos, cyanide — not biodegradable, persistent, some subject to biomagnification
Halogenated aliphatics	Used in fire extinguishers, refrigerants, propellants, pesticides, solvents, and in dry cleaning — can cause damage to central nervous system and liver
Ethers	Used mainly as solvents for polymer plastics — carcinogens
Phthalate esters	Used chiefly in production of polyvinyl chloride and thermoplastics as plasticizers — can be teratogenic and mutagenic in low concentrations
Monocyclic aromatics (excluding phenols, cresols, and phthalates)	Used in the manufacture of other chemicals, explosives, dyes and pigments, and in solvents, fungicides, and herbicides — central nervous system depressant, can damage liver and kidneys
Phenols	Chiefly used as chemical intermediates in the production of synthetic polymers, dyestuffs, pigments, pesticides and herbicides — toxicity increases with degree of chlorination, can impart objectionable odors and taste to drinking water
Polycyclic aromatic hydrocarbons	Used as dyestuffs, chemical intermediates, pesticides, herbicides, motor fuels, and oils — carcinogenic in animals, indirectly linked to cancer in humans
Nitrosoamines	Used in the production of organic chemicals and rubber — tests with laboratory animals indicate nitrosoamines are some of the most potent carcinogens

the laboratory BOD test and the real environment. BOD data are used routinely to measure the pollutional strength of wastewaters, to design biological treatment processes, and to measure the performance of treatment facilities.

Chemical oxygen demand (COD) is a chemical oxidation test used to estimate the total oxygen demand of a wastewater. The test is based on the fact that with few exceptions, organic compounds can be oxidized by strong oxidizing agents under acid conditions with the assistance of inorganic catalysts. The COD test measures biodegradable organic compounds, organics resistant to biological oxidation, and those that may be toxic to the organisms used in the BOD test.

The total organic carbon (TOC) and total oxygen demand (TOD) tests also measure organic matter in wastewater. The TOC is measured by oxidizing organic

Table 2. Methods for the Identification of Organics in Wastewater

Method	Remarks
BOD Biochemical oxygen demand	— measures biodegradable compounds under conditions related to those that occur in nature — measures the oxygen required by bacteria as they metabolize the organics — a general, nonspecific parameter
COD Chemical oxygen demand	— estimates the oxygen demand using strong oxidizing agents, acid conditions, and certain inorganic catalysts — measures biodegradable and many nonbiodegradable organic compounds — a general, nonspecific parameter
TOC Total organic carbon	— measures organic carbon using high temperatures and a catalyst
TOD Total oxygen demand	— measures the oxygen required for the combustion of organics at high temperatures and with a catalyst
GC, HPLC, MS Gas chromatography, High performance liquid chromatogaphy, Mass spectroscopy	— identifies specific organic compounds including those that are nonbiodegradable and that have been designated as priority pollutants

carbon to carbon dioxide in a high-temperature furnace in the presence of a catalyst. The TOD test measures the amount of oxygen required for the combustion of impurities in an aqueous sample at a high temperature using a platinum catalyst. The oxygen demand of carbon, hydrogen, nitrogen, and sulfur in a wastewater sample can be measured by the TOD test.

BOD, COD, and TOD utilize an oxygen approach while TOC uses a carbon approach to the measurement of organics in wastewaters. There are no fundamental correlations among the measurements. However, when wastes have reasonably uniform characteristics, there can be a fairly constant relationship between BOD and the other measurements. Once such a relationship is established, COD, TOC, or TOD can be used in place of BOD for routine monitoring.

An important difference in these measurements is that the BOD test is an attempt to indicate the impact of biodegradable organic matter on the aquatic ecosystem. COD, TOC, and TOD measure both biodegradable and nonbiodegradable organics.

Nonbiodegradable and Toxic Organics

Gross values of organic substances such as BOD, COD and TOC are of little value where there is a need to identify specific organic compounds in a wastewater. No general method, comparable to the BOD test for biodegradable organics, has been developed to measure nonbiodegradable or toxic organic compounds in wastewaters. Narrow spectrum or single-chemical methods of analysis have been developed to measure priority pollutants and other specific organic pollutants. In addition, broad spectrum measurement methods are being developed to quantify a range of specific chemicals or classes of chemicals found in industrial wastewaters and treated effluents.

Guidelines establishing test procedures for 113 organic toxic pollutants are available[8]. For each pollutant, two acceptable methods are proposed: (a) either gas chromatography (GC) with selected detectors or high performance liquid chromatography (HPLC) depending on the particular pollutant, and (b) GC coupled with MS.

Analytical methods for nonbiodegradable and toxic organic compounds continue to undergo refinement and evaluation. Sophisticated and expensive analytical equipment is necessary for the GC, MS, and HPLC methods. In spite of these limitations, both single-chemical and broad spectrum analytical methods will see increasing use.

Historical Data Base

Standardized analytical methods have been used for BOD since the 1940's, COD since the 1950's and TOC since the 1960's. Thus, information on the concentration of organic substances as measured by these parameters has been available for decades. At many industrial plants, untreated and treated wastewaters are analyzed for one or more of these parameters at least weekly, and in some cases, every day. As a result, a significant historical data base is available on the BOD and COD characteristics of untreated industrial wastewaters and on the reduction that occurs in biological and other treatment processes. This data base has proven valuable in developing technology-based effluent limitations and in identifying effluent characteristics from various treatment processes.

In contrast, interest in nonbiodegradable and toxic organic pollutants has been so recent that there is only a small historical data base on the occurrence of these organics in industrial wastewaters and their reduction in biological and other treatment processes. Although there has been long-term interest in the measurement of some organic compounds such as phenol and certain pesticides, only since about 1978 have efforts been initiated to identify organics such as the priority pollutants in industrial wastewaters. EPA now has a strong effort to acquire information on the occurrence of priority pollutants in wastewaters and their removal by treatment processes.

Relative Concentrations of Organic Pollutants

Concentrations of conventional and nonconventional pollutants in industrial wastewaters usually are measured in terms of milligrams per liter (mg/L), whereas the concentrations of priority pollutants are measured in terms of micrograms per liter (μ/L). In the effluent of many municipal and industrial wastewater treatment systems, a number of the priority pollutants are either not detected or are found only at about the levels of detectability for the analytical methods that were used.

BIOLOGICAL TREATMENT

General

Biological treatment, the microbial degradation of organics, is a process that occurs throughout nature. Uncontrolled biological treatment occurs in streams, soils, and swamps while controlled biological treatment processes occur in man-made treatment tanks and systems. The controlled processes are designed to accomplish a required amount of organic matter removal from wastewaters.

Because microorganisms are the key to the success of biological treatment processes, an understanding of the processes must be based upon microbiological fundamentals, and on the microbial transformations that occur in the biological treatment units. If this understanding can be achieved, rational predictions of performance become possible, and the capabilities of a process can be better utilized. Without a sound understanding of the fundamentals, the processes can be treated only as "black boxes" in which the performance is subject to parameters seemingly out of man's control. In such cases, successful design and operation can be based only on prior performance of similar processes. Such performance may be difficult to transfer to different wastes and environmental conditions.

The objectives of biological treatment are to stabilize, coagulate and remove the soluble, colloidal, and suspended organics in wastewater. Until the past few decades, the concepts relating to the biological oxidation of organics were developed either from the treatment of domestic wastewater, or from the oxidation of simple chemical substrates such as glucose. Industrial wastes can have different characteristics, and direct application of such design and performance data to the full-scale treatment of industrial wastes is not always possible. Fortunately, many industrial wastewaters have now been treated using biological treatment processes and successful design and operational criteria have evolved for the biological treatment of industrial wastes.

The removal of organics in biological treatment processes is related to the characteristics of the wastes. Suspended solids are incorporated in the microbial floc and are removed by flocculation and settling. Colloidal matter can be adsorbed on the microbial surfaces. The biodegradable organics are metabolized by the microorganisms. High levels of organic removal are related to the type, composition, and the concentration of the organics present.

This section summarizes some of the key factors that influence the performance of biological treatment processes and describes common biological treatment systems.

Important Factors

The performance of biological treatment processes is influenced by those factors that affect the microorganisms in the processes. These include temperature, solids-retention time, nutrients, oxygen, pH, and inhibition and toxicity.

To reproduce and function, microorganisms must have a source of energy, carbon, nutrients such as nitrogen and phosphorus, and trace elements for cell synthesis. Carbon dioxide and organic carbon are the sources of carbon used by microorganisms. If an organism obtains its carbon from organic carbon, it is heterotrophic; if it uses carbon dioxide it is autotrophic. The overwhelming majority of microorganisms in biological waste systems are heterotrophic.

Temperature—

Variations in temperature affect biological processes by influencing the metabolic activities of the microorganisms, the transfer of oxygen and other gases, and the settling characteristics of biological solids. According to the temperature range in which they function best, microorganisms may be classified as psychrophilic, mesophilic, and thermophilic. The optimum temperature ranges for these microorganisms are 12° to 18° C, 25° to 40° C, and 55° to 65° C, respectively. Almost all biological waste treatment processes operate in the mesophilic range. With the exception of certain anaerobic treatment systems, temperature is not controlled in biological treatment processes.

The effect of temperature on the reaction rate of a biological treatment process is commonly expressed as:

$$k_{T_2} = (k_{T_1})\, \theta\, (T_2 - T_1)$$

where T_1 is the temperature of reaction rate kT_1, T_2 is a different temperature at which the rate kT_2 is desired, and θ is the temperature coefficient. θ values are generally in the range of 1.04 to 1.10. If $\theta = 1.072$, a reaction rate is doubled for an increase in temperature of 10°C. This has led to the generalization that biological reaction rates are doubled for each 10°C rise in temperature. This estimation is useful for temperatures around 20°C and is less applicable at extreme temperatures.

In a biological treatment process, the reduction of the temperature by about 10°C will require about twice as many active organisms in the process to achieve equivalent process efficiencies. This can be accomplished by increasing the mixed liquor suspended solids (MLSS) concentration thereby increasing the microbial solids retention (SRT) of the unit. Systems with solids recycle permit the operator to compensate for lower temperatures by increasing the microbial solids in the unit. Systems without solids recycle do not have this flexibility.

Solids Retention Time—

Fundamentally,

$$\text{SRT} = \frac{\text{weight of microorganisms in the system}}{\text{weight of microorganisms leaving the system per unit time}}$$

SRT should be determined using the quantity of active organisms in the system. However, measuring the active microbial mass in a biological treatment unit is difficult and other parameters are used. Assuming that complete mixing and therefore uniform distribution of the active microorganisms and other solids occurs, SRT can be determined in terms of parameters such as volatile suspended solids, total suspended solids, or total solids. Thus SRT can be defined by

$$\text{SRT} = \frac{(X_a)V}{\Delta X}$$

where X_a = average mixed liquor volatile or total suspended solids, mass per reactor volume (such as grams per liter), V = unit volume (such as liters), and ΔX = solids loss or wastage, mass per day (such as grams per day).

The actual SRT of a biological treatment system must be greater than the minimum time it takes for the organisms to reproduce in the system. If this does not occur, the microorganisms will be removed from the system in the effluent at a faster rate than they can multiply, and failure of the biological system will result. The minimum or critical SRT (SRT_c) is that SRT at which a stable microbial cell population can be maintained. The SRT_c for biological processes ranges from 2 to 6 days for anaerobic systems and from 0.1 to 0.4 days for aerobic systems. The range of SRT_c values is a result of the impact that other process variables, such as temperature and inhibition, have on microbial growth. Temperature and SRT_c are interrelated, with SRT_c increasing as the temperature decreases.

Preliminary treatability studies are important with industrial wastes to establish design parameters and the relationship of SRT and other control parameters to desired effluent quality and process performance.

Nutrients—

To achieve satisfactory biological treatment, the wastewaters being treated must contain sufficient basic nutrients such as carbon, nitrogen, phosphorus, and trace minerals to sustain the desired rates of microbial activity. Certain industrial wastes may not be nutritionally balanced.

The common approach of avoiding nitrogen or phosphorus limitations in aerobic systems is to add these nutrients to obtain a BOD:N:P ratio of 100:5:1. This assures that there is no deficiency of these nutrients and will result in measurable amounts of nitrogen and phosphorus in the effluent. Studies with nutrient deficient wastes have established that 3-4 kg N per 100 kg BOD_5 removed and 0.5-0.7 kg P per 100 kg BOD removed will avoid nutrient deficient conditions. This results in a BOD:N:P ratio of about 100:3:0.6 and assures minimum nitrogen and phosphorus in the effluent.

Oxygen—

Aerobic biological treatment processes require adequate oxygen input to meet the needs of the microorganisms. The total oxygen requirements are related to the oxygen needed for: (a) biological oxidation of the carbonaceous organics (O_C), (b) biological oxidation of the organic and ammonia nitrogen (O_N), (c) endogenous respiration of the biomass (O_E), and (d) any immediate oxygen demand. Not all of these oxygen demands occur in every biological treatment process. The actual oxygen demand is related to the characteristics of the wastewater and the desired effluent quality. As a minimum, oxygen is needed to meet the carbonaceous and endogenous requirements.

pH—

The pH in the biological treatment process will affect the growth of the microorganisms. Organisms in the treatment systems normally will not function at pH levels above 9.5 or below 4.0. The optimum pH range for most treatment systems is about 6 to 8. The most critical pH is that of the mixed liquor in contact with the organisms and not that of the entering wastewater. The entering wastewater will be diluted by the aeration tank contents and partially neutralized by the buffer capacity of the mixed liquor. When there is inadequate buffering capacity in the unit, acidic and caustic industrial wastewaters must be neutralized before being treated in a biological unit.

Inhibition and Toxicity—

Compounds that inhibit or retard the metabolism of the microorganisms can affect the performance of biological treatment processes. Certain cations, such as lead, copper, and arsenic, and certain anions, such as cyanides and fluoride, can be toxic to microorganisms. Some organic compounds in industrial wastewaters also can be toxic. Treatability studies can identify whether industrial wastes are inhibitory to biological systems and the relative degree of inhibition.

Biological Treatment Processes

There are many types of biological treatment systems that can be used for wastewater treatment. These can be defined by the presence or absence of oxygen, i.e., aerobic or anaerobic, by their photosynthetic ability, or by the mobility of the organisms, i.e., suspended or attached growth. The major biological treatment processes are identified in Table 3 and examples described below.

Activated Sludge—

Activated sludge processes are widely used to treat municipal and industrial wastes since they are versatile, flexible, and can be used to produce an effluent of desired quality by varying process parameters. The process was so-named because it produces an active mass of microorganisms capable of aerobically stabilizing a waste. Many versions of the basic process exist but all are fundamentally similar.

The term activated sludge is applied to both the process and to the biological solids in the treatment unit. The mixed liquor suspended solids or activated sludge contains a variety of heterotrophic microorganisms such as bacteria, protozoa, fungi, and

Table 3. Common Biological Treatment Processes

- Aerobic
  - Activated sludge
  - Trickling filters
  - Aerated lagoons
  - Oxidation ditch
  - High rate algal ponds
  - Rotating biological contactors
- Facultative
  - Oxidation ponds
- Anaerobic
  - Anaerobic lagoons
  - Anaerobic filters
  - Digesters
  - Anaerobic contact process

- Suspended Growth
  - Activated sludge
  - Aerated lagoons
  - Oxidation ditch
  - Mixed digesters
- Attached Growth
  - Trickling filters
  - Packed bed reactors
  - Anaerobic filter
  - Rotating biological contactors
- Photosynthetic
  - Oxidation ponds
  - High rate algal ponds

larger microorganisms. The predominance of a particular microbial species depends upon the waste that is treated and the way in which the process is operated.

The microorganisms will aggregate into flocculant masses which can be kept in suspension while the activated sludge is mixed but which will settle when the mixing is stopped. These properties are important because they permit the microbial solids to mix with the influent wastewater yet separate readily in a subsequent separation unit. A well-treated effluent containing few suspended solids will result.

The system shown in Fig. 3 illustrates the components of an activated sludge system. This system incorporates recycle of the settled microbial solids to the aeration basin to maintain a high microbial population and a long SRT to treat the settled wastewater. Excess waste activated sludge and settled solids from the primary clarification units are sent to an anaerobic or aerobic digester for stabilization prior to final disposal. The aeration unit is maintained aerobic by diffused or mechanical aeration which also serves to mix the contents of the unit.

Aerated Lagoons—

Aerated lagoons are similar to an activated sludge unit in that oxygen is supplied continuously by mechanical or diffused aeration. An aerated lagoon is essentially the same as a long SRT activated sludge system except that a shallow (8 to 10 ft) earthen basin serves as the reactor, primary clarification may not be used before the wastewaters enter the aerated lagoon, a separate final clarification unit may not be used and solids recycle does not occur. When final clarification is not used, the effluent end of the aerated lagoon is not well mixed and many of the mixed liquor solids settle out in the lagoon.

The aerated lagoon contains fewer microbial solids than an activated sludge unit and mixing may not be sufficient to keep all of the solids in suspension. A schematic of an aerated lagoon is shown in Fig. 4.

The lagoon temperature depends upon the mixing that takes place and the rate at which heat is lost. Because of the large surface area and the long liquid detention time, the lagoon temperature can be close to the ambient air temperature.

Aerated lagoons require more land area but less care and maintenance than activated sludge systems and are commonly used by many industries.

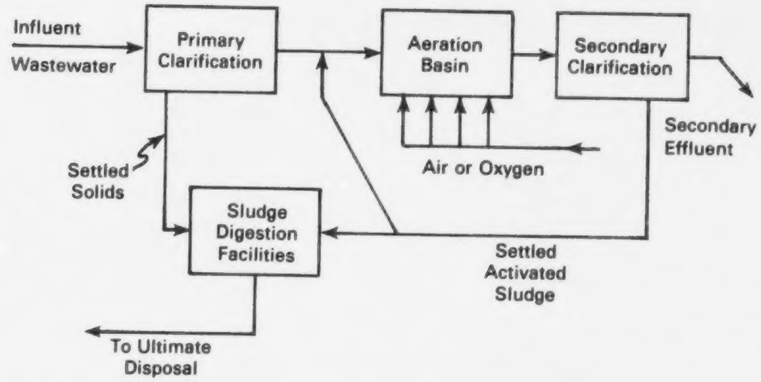
Influent
Wastewater
Primary Clarification
Aeration Basin
Secondary Clarification
Secondary Effluent
Air or Oxygen
Settled Solids
Sludge Digestion Facilities
Settled Activated Sludge
To Ultimate Disposal

Figure 3. Components of an activated sludge system.

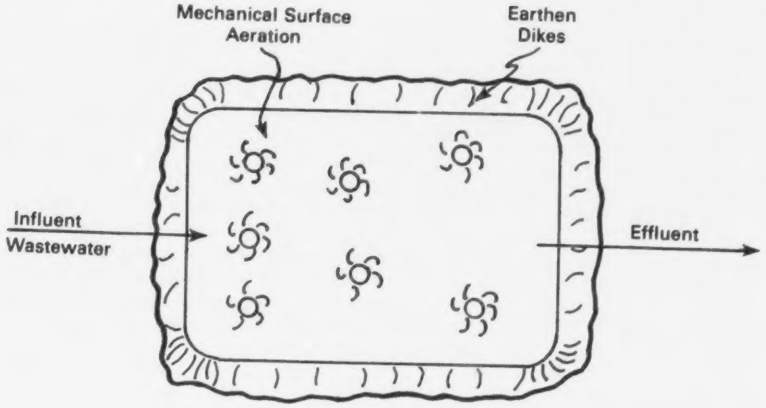
Mechanical Surface Aeration
Earthen Dikes
Influent
Wastewater
Effluent

Figure 4. Schematic top view of an aerated lagoon.

Oxidation Ponds—

Oxidation ponds are the simplest aerobic biological treatment process used to treat wastewaters. Fig. 5 portrays the processes that take place in an oxidation pond. The pond effluent contains bacteria, algae, and soluble organic and inorganic compounds.

These ponds are relatively shallow, diked structures with a large surface area. No mechanical aeration is used, and the aerobic conditions are a result of photosynthetic algae and wind action. Where land is relatively flat, inexpensive, and available, oxidation ponds can be more economical than other types of aerobic biological treatment. They generally are used in rural areas with adequate sunlight, wind action, and available land. They have been used for the treatment of

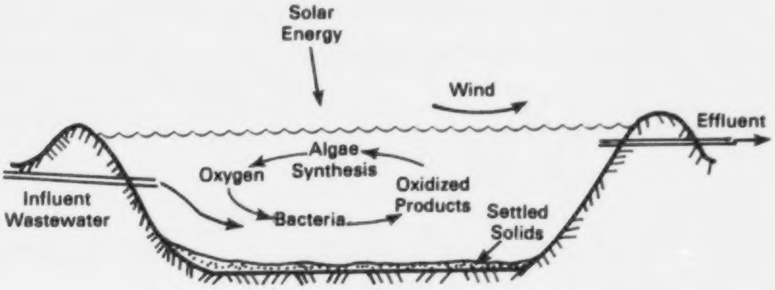

Figure 5. Schematic cross-section of an oxidation pond.

petroleum refining and petrochemical wastewaters as well as wastewaters from food processing, textile, pulp and paper and other industries.

An activated sludge unit, an aerated lagoon and an oxidation pond used to treat the same wastes will differ greatly in size, as well as in the control that can be exerted over the units. The environment within an oxidation pond cannot be controlled by the operator or design engineer. Only physical factors such as size or loading rate can be controlled, and reliance is placed upon natural microbial reactions. In aerated lagoons, mechanical aeration is provided. With an activated sludge system, the degree of aeration and mixing, solids recycle and the mixed liquor solids concentration all can be controlled closely.

These relative levels of control are manifest in the different liquid detention times that occur in each unit. Table 4 indicates the period of time that a volume of liquid (liquid detention time) will stay in the respective units.

The term "aerobic" does not completely describe the microbial reactions that take place in an oxidation pond. While ample dissolved oxygen may exist in the upper portion of the pond, there may be little or no dissolved oxygen in the lower depths. Oxidation ponds are designed and loaded so that the anaerobic conditions in the lower portions have little impact on the quality of effluent from the ponds.

Both bacteria and algae are key microorganisms in an oxidation pond. Soluble organics in the pond are metabolized by the bacteria and end products of that metabolism, such as carbon dioxide, ammonium and nitrate ions, and phosphate ions, become available for growth of the algae. As the autotrophic algae generate new cells using solar energy, oxygen is produced which can be used by the hetrotrophic bacteria. Surface reaeration due to wind action rarely can meet the oxygen needed for the oxidation of the organic matter in the pond, and the oxygen produced by the algae is essential to maintain aerobic conditions.

Trickling Filters—

Trickling filters are an aerobic attached growth biological process. They are not filters but are aerobic oxidation units which absorb and oxidize the organic matter in the wastewater which passes over the microorganisms on the permeable media. Trickling filters consist of a bed of media to which microorganisms attach and over which the wastewater passes. The media generally used are stone or rock of large size (2 to 4 inches, 50 to 100 mm) or plastic or wood of various configurations.

The waste to be treated is distributed over the top of the media by a movable, generally a rotary, distributor. Trickling filters are designed to treat liquid wastes with few solids. Readily settleable solids are removed in a primary treatment unit before the wastewaters are treated in a trickling filter.

Table 4. Range of Liquid Detention Times in Different Biological Treatment Units

Unit	Detention Time (days)
Activated sludge	0.2-1
Aerated lagoon	5-10
Oxidation pond	20-60+

The organic matter in the wastewater is removed by the population of microorganisms that are attached to the media. As the microorganisms grow, the thickness of the microbial layer increases, and microbial solids periodically wash off, permitting a new microbial layer to grow. The solids in the trickling filter effluent are removed in a secondary sedimentation unit. A flow diagram of a trickling filter system is shown in Fig. 6.

The trickling filter media are supported on an underdrain system which collects the treated wastewater and microbial solids from the filter for transport to the secondary sedimentation unit. The underdrain assists in keeping the filter aerobic by facilitating air movement through the filter.

In contrast to an activated sludge system, there is little opportunity to increase the microbial solids in a trickling filter above that which would be there normally. The return of settled microbial solids from the secondary clarifier, as in an activated sludge system, can clog the openings in the filter media and impair the filter performance.

With proper design and concern about inhibitory compounds and consistent loading, trickling filters can successfully treat many industrial wastes.

PACT Process—

Biological treatment does not remove nonbiodegradable and toxic compounds unless such compounds become part of the microbial floc or are removed in the clarification systems. The PACT process is a patented process that incorporates powdered activated carbon in the biological treatment unit (Fig. 7). The activated carbon adsorbs many organics not readily biologically degradable and that otherwise may not be removed. The process also aids the removal of BOD, COD, and color. Carbon dosages have ranged from 15 mg/L to 200 mg/L of influent wastewater.

The process has been used successfully with several industrial wastes including those from the manufacture of complex organic chemicals and from oil refining. In one full-scale study[2], greater than 82% removal of the priority pollutants was achieved with the PACT process. With a carbon dosage of 100 mg/L, 99.6% removal of benzene and 84% removal of 2,4-dichlorophenol was achieved.

Sedimentation—

In all treatment systems, clarification units are an important component (Figs. 1, 3, 6, 7). The majority of these units are gravity sedimentation units. Separate units are needed to remove: (a) readily settleable organic solids that would add an additional load to the subsequent biological units or would impair the performance of units such as a trickling filter, and (b) the settleable microbial solids synthesized in the biological units. To achieve the desired effluent quality, a biological treatment system must include properly designed and operated secondary solids sedimentation units.

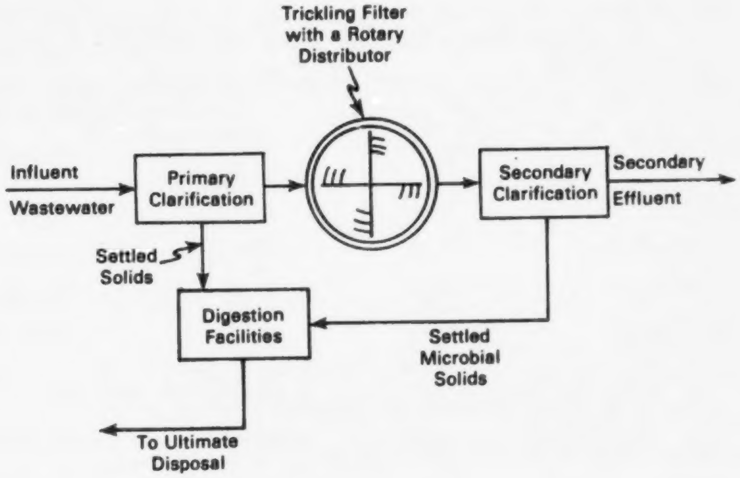
Trickling Filter with a Rotary Distributor
Influent
Wastewater
Primary Clarification
Secondary Clarification
Secondary
Effluent
Settled Solids
Digestion Facilities
Settled Microbial Solids
To Ultimate Disposal

Figure 6. Components of a trickling filter system.

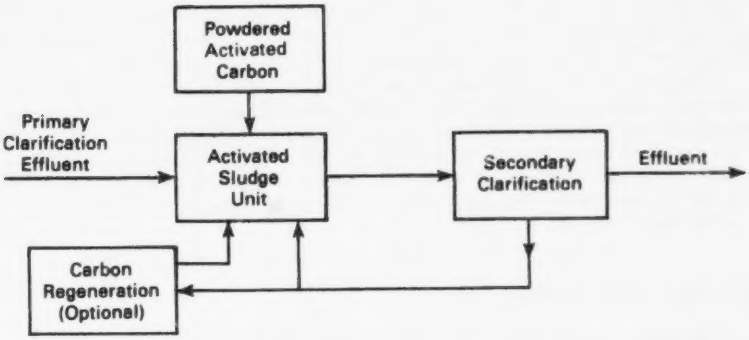
Powdered Activated Carbon
Primary Clarification Effluent
Activated Sludge Unit
Secondary Clarification
Effluent
Carbon Regeneration (Optional)

Figure 7. Schematic of the PACT process in which activated carbon is added to an activated sludge unit.

Effluent Quality—

Well-designed and well-operated biological treatment facilities are capable of a high degree of organic removal and low concentrations of organics in the treatment plant effluent. Because processes such as aerated lagoons and oxidation ponds normally do not have secondary clarification units, the effluent from such processes will have higher concentrations of solids and associated BOD than will processes such as activated sludge systems and trickling filters. Table 5 indicates the type of BOD removals and effluent quality that result with the biological treatment systems discussed previously.

Table 5. Typical Range of BOD Removals and Effluent BOD and Suspended Solids Concentrations for Biological Treatment Systems*

	BOD Removal (%)	Effluent Concentrations (mg/L)	
		BOD	Suspended Solids
Activated sludge	85-95+	5-25	10-30
Trickling filter	85-95	5-25	10-30
Aerated lagoon	80-95	30-80	60-200**
Oxidation pond	75-95	30-80	60-150**

* Actual removals and effluent concentrations are related to system design and operation and influent wastewater characteristics.

**These solids consist of microorganisms, inert material and algae; the concentration depends on the amount of settling that takes place prior to discharge.

Variability of raw waste flow and characteristics, and changes in process temperatures can affect the effluent quality from industrial waste treatment systems. The impact of these factors is more pronounced with systems that have short solids and hydraulic retention times and low concentrations of microorganisms. Increased BOD loads can affect performance of the biological units by creating oxygen demands in excess of the aeration system oxygen transfer capabilities. Adverse effects from toxicants, salts, nutrient shortages, and temperature changes can be heightened at marginal dissolved oxygen levels in the biological units.

There are, however, approaches that can minimize effluent variability. Table 6 indicates several possibilities. Many of these are necessary to achieve consistent and satisfactory performance by industrial waste treatment plants. Especially effective are: (a) monitoring of the influent so as to adjust plant operation when there are large variations in pH, flow, toxic compounds, and organic load, (b) equalization basins or tanks, (c) proper operation of the biological process, and (d) flexibility to utilize solids recycle.

Pollutant Removal Mechanisms

Removal of pollutants in a treatment system occurs as a result of physical, chemical, and biological processes that occur within the system. Although aerobic biological treatment systems are designed to remove soluble organics by microbial degradation, there actually are several removal mechanisms that take place: microbial degradation, air-stripping and volatilization, and adsorption on the sludge (Fig. 8). Other possible mechanisms include hydrolysis and photolysis, but these play a minor role in biological treatment processes.

Air-stripping and adsorption can be important removal mechanisms for organic compounds that may not be readily biodegradable but may have high volatility or high adsorption characteristics for the microbial sludge respectively. While air-stripping and adsorption can be important mechanisms to remove organic chemicals from industrial wastewater and to meet effluent limitations, they merely transfer the pollutants to another media, i.e., the atmosphere and the sludge. In solving one problem, care must be taken to avoid exacerbating or creating other problems. Thus it is important to comprehend how pollutants are removed in biological treatment systems.

Table 6. Approaches to Minimize Effluent Variability

- Monitoring of process discharges
- Holding and blending waste streams before discharge
- Separate treatment of problem process wastewaters
- Automated monitoring of influent quality
- Equalization basins
- Control of biomass concentrations and recycle
- Ability to control adverse pH levels
- Adequate oxygen supply

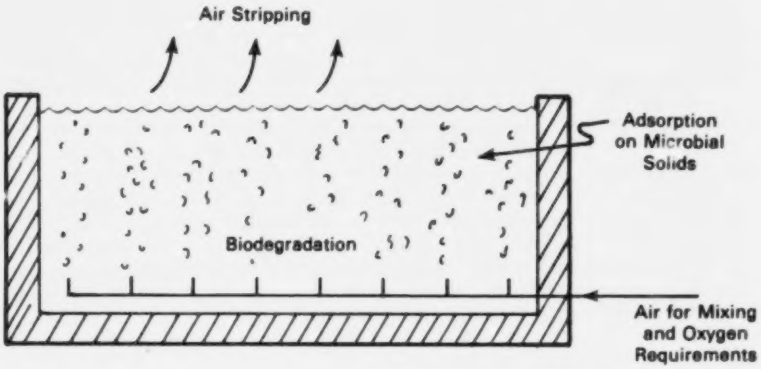
Air Stripping
Adsorption on Microbial Solids
Biodegradation
Air for Mixing and Oxygen Requirements

Figure 8. Mechanisms for pollutant removal in biological treatment processes.

Aeration—

Aeration in biological treatment units provides air-liquid contact and an opportunity for the transfer of volatile organic compounds from the liquid phase to the gas phase. Stripping of organic compounds by aeration may result wherever significant surface turbulence occurs such as caused by mechanical aeration, spraying, or bubble diffusion. Many organic compounds discharged in wastewaters from the organic chemicals industry are air-strippable[3]. The removal of an organic by aeration is governed by two major factors: (a) the tendency of a compound to establish an equilibrium between the gas and liquid phases, and (b) the intensity and duration of the aeration.

Adsorption on Sludge—

Adsorption of organics on sludge provides an additional removal mechanism in biological treatment systems. Primary sludge, mixed liquor suspended solids, and secondary sludges have surface areas which favor sorption of organics. Organics which are insoluble or only slightly soluble can be sorbed to these surfaces and can be removed in a biological treatment process even though the amount of their biodegradation may be small. As an example, pesticides have been found to accumulate in grease scum layers. The factors affecting sorption include solubility, pH, concentration, temperature, molecular weight and available surface area.

Microbial Degradation—

The factors affecting the microbial degradation of organics in biological treatment systems have been discussed earlier. These include solids retention time, nutrients, oxygen, pH, inhibition, toxicity and acclimation. Several control approaches can be used to optimize microbial degradation. Those commonly in use center on: (a) maintaining proper solids retention time to achieve the desired degradation, (b) acclimatizing the microorganisms to the organic compounds, and (c) maintaining proper nutrient and oxygen balances.

MUNICIPAL WASTE TREATMENT

General

Publicly owned treatment works (POTWs) treat the combined domestic, commercial and industrial wastes of a community. As a result, conventional, non-conventional and priority pollutants can be present in the POTW influent. POTWs are designed to remove conventional pollutants. Generally, they accomplish 85% or better removals of BOD and suspended solids.

Although POTWs are not designed to remove toxic pollutants, in many cases high removals do occur. Those priority pollutants that can be (a) volatilized or degraded in the biological treatment units, (b) sorbed to the biological solids, and (c) deposited in the primary or secondary sedimentation units may be removed substantially.

Since about 1977, considerable effort has been directed to determining how effectively POTW biological processes remove priority pollutants. These efforts include: (a) an extensive EPA sampling and analysis program to evaluate the occurrence and fate of priority pollutants in 40 POTWs and (b) research activities geared to provide additional removal and occurrence information. This section summarizes the results that have been obtained.

The 40 City Study

From 1978 to 1980, EPA conducted a study of the occurrence and fate of priority pollutants in 40 POTWs. The first phase was a two-plant pilot study designed to set operating parameters for the remainder of the study. In 1980, EPA published an interim report[4] which summarized data from the two POTWs evaluated in the pilot study plus eighteen additional POTWs. At the time that this section was written, only the interim report was available. It is understood that the complete study which will include results from all 40 POTWs is to be published later in 1982.

All of the POTWs had common secondary treatment processes with activated sludge and trickling filters being the most common. While few of the POTWs had effluents that always met secondary treatment requirements (30 mg/L BOD and 30 mg/L total suspended solids), the POTWs included in the study were selected only if their operation was considered to be reasonably good. Therefore, the results of the study can be considered as coming from well-operated plants.

At each plant, a minimum of six days of 24 hour sampling of influents, effluents and sludges was completed. Each sample was analyzed for conventional and priority pollutants as well as selected non-conventional pollutants.

Combining data from all liquid and sludge samples, 103 priority pollutants, including metals, were detected at least once. The organic priority pollutants not detected were acrolein, benzidine, hexachloroethane, hexachlorocyclopentadiene, nitrobenzene, several ethers, all nitrosoamines, endosulfans and metabolites, endrin and metabolites, all but two PCB mixtures, and toxaphene.

Table 7 identifies the organic priority pollutants that were found in at least 25% of the influent samples and Table 8 identifies the organic priority pollutants that were

Table 7. Occurrence* of Organic Priority Pollutants in POTW Influent Samples[4]

Chemical	Percent of Times Detected	Range of Concentrations Detected (μg/L)
Toluene	98	2 - 500
Tetrachloroethylene	97	2 - 1,100
Chloroform	96	1 - 430
Methylene chloride	95	1 - 11,000
Trichloroethylene	95	1 - 860
Bis (2-ethylhexyl) phthalate	94	2 - 390
1,1,1-Trichloroethane	91	1 - 1,600
Ethylbenzene	86	1 - 448
Phenol	83	1 - 380
Benzene	68	1 - 1,560
Di-n-butyl phthalate	63	1 - 105
Diethyl phthalate	62	1 - 33
Butyl benzyl phthalate	59	2 - 140
1,2-Trans-dichloroethylene	58	1 - 97
Naphthalene	55	1 - 150
1,1-Dichloroethane	40	1 - 24
1,1-Dichloroethylene	35	1 - 243
1,2-Dichlorobenzene	30	2 - 440
Pentachlorophenol	27	2 - 94
Anthracene	27	1 - 93
Phenanthrene	27	1 - 93

*Found in at least 25% of the influent samples.

Table 8. Occurrence* of Organic Priority Pollutants in POTW Effluent Samples[4]

Chemical	Percent of Times Detected	Range of Concentrations Detected (μg/L)
Bis (2-ethylhexyl) phthalate	91	2 - 370
Methylene chloride	88	1 - 1,570
Chloroform	88	1 - 61
Tetrachloroethylene	82	0 - 320
Di-n-butyl phthalate	59	1 - 92
1,1,1-Trichloroethane	57	1 - 370
Trichloroethylene	54	1 - 97
Toluene	48	0 - 1,100
Gamma — BHC	36	0.01 - 0.84
Phenol	27	1 - 89

*Found in at least 25% of the effluent samples.

found in at least 25% of the effluent samples. Two facts are obvious from the information in these tables. First, the concentrations of organic priority pollutants in wastewater influents and effluents are at least three orders of magnitude less than the concentrations of conventional pollutants in similar wastewaters. For example, the concentration of BOD and suspended solids in untreated municipal wastewater is in the range of 150-300 mg/L. In the effluent of secondary treatment plants, both BOD and suspended solids concentrations are in the 20-40 mg/L range. The tables show the influent and effluent concentrations of priority pollutants are generally in the 0.001 to 1 mg/L (1 to 1000 μg/L) range.

Second, the organic priority pollutants were found less frequently in the effluent. The decrease in frequency is expected since a number of mechanisms can remove such pollutants in POTWs.

Not all of the organic priority pollutants were degraded microbially or were volatilized. Many were sorbed to solids and settled in the primary and secondary clarifiers to become part of the sludge. Table 9 identifies the organic priority pollutants that were found in at least 25% of the samples of untreated sludges. Many of the organic compounds were concentrated in the sludges and were found here with greater frequency than in the plant influent or effluent.

Because many of the organic priority pollutants were detected in the influent and effluent wastewater at concentrations only barely above detection limits, percent removals of only a few of the organic compounds could be determined. Table 10 summarizes data for the organic compounds for which there were 10 or more usable data points to determine percent removals. For purposes of comparison, percent removals of organics as measured by common parameters are also included in Table 10.

On the average the POTWs achieved high BOD and suspended solids removals (91 and 92% respectively). The removals of the organic priority pollutants were variable, as high as 94% for toluene and as low as 55% for methylene chloride. It must be noted that the POTWs were designed and operated to remove conventional pollutants (BOD and suspended solids) rather than the priority pollutants.

Other Studies

Information is available on the removal of PCB compounds in POTWs[5]. A survey of PCBs in the wastewaters of 33 municipalities and of their fate during conventional secondary treatment showed the following: PCB concentrations in untreated wastewaters ranged from less than 0.1 to 1.8 μg/L; primary treatment removed, on the average, 50% of the PCB load, and secondary systems averaged 66% removal; PCB concentrations in digested sludges ranged from 0.6 to 76.6 ppm (dry weight); PCB removal during wastewater treatment occurred largely by accumulation in the primary and/or waste activated sludge.

The behavior and fate of twenty-two potentially toxic organic compounds[6] was evaluated in a small scale pilot plant that had treatment facilities comparable to those at a POTW secondary treatment plant. The 22 compounds consisted of four pesticides, three phenols, six phthalates and nine polynuclear aromatic hydrocarbons (PAHs). The compounds were added to typical municipal wastewater to obtain a concentration of about 50 μg/L of each compound. Removals of the compounds were typically in the 95-98 percent range and the activated sludge effluent concentrations generally were less than 10 μg/L with many concentrations less than 3 μg/L. Many of the compounds were concentrated in the sludges.

Summary

The data indicate that: (a) well operated POTWs remove variable but significant removals of organic priority pollutants, (b) POTW effluents contain some organic priority pollutants in low concentrations (generally less than 100 μg/L), and (c) many of the priority pollutants can be found in POTW sludges.

Table 9. Occurrence* of Organic Priority Pollutants in Untreated POTW Sludges[4]

Chemical	Percent of Times Detected	Range of Concentrations Detected (μg/L wet weight)
Toluene	95	1 - 42,300
Bis (2-ethylhexyl) phthalate	95	20 - 35,000
Ethylbenzene	73	1 - 4,200
Benzene	69	1 - 694
Methylene chloride	63	1 - 3,310
1,2-Trans-dichloroethylene	62	1 - 96,000
Anthracene	53	6 - 3,200
Phenanthrene	53	6 - 3,200
Phenol	52	19 - 17,000
Trichloroethylene	50	1 - 4,690
Pyrene	46	6 - 1,700
Di-n-butyl phthalate	45	14 - 1,600
Butyl benzyl phthalate	42	1 - 45,000
1,1-Dichloroethane	42	1 - 2,880
Tetrachloroethylene	37	1 - 2,800
Fluoranthene	34	8 - 1,200
Naphthalene	33	11 - 5,200
1,2-Benzanthracene	26	9 - 1,500
Chrysene	25	9 - 1,500

*Found in at least 25% of the sludge samples; some of the sludges were mechanically thickened sludges.

INDUSTRIAL WASTE TREATMENT

General

Biological treatment is used to treat many industrial wastewaters and achieve the effluent quality necessary to meet BPT limitations. Process performance commonly is measured in terms of the concentration of BOD, COD, suspended solids and other pollutant parameters in the effluent or of percent reduction of these parameters. As a result, most of the existing information on the removal of organics from industrial wastewater relates to the removal of conventional pollutants. In recent years, however, many studies have been directed to the removal of priority and non-conventional organic pollutants in industrial treatment systems. The following examples describe the performance that has been achieved.

Chemical Industry

A study of wastewater treatment facilities at five chemical industry plants was designed to evaluate the effectiveness of biological treatment in removing toxic pollutants in wastewaters that result from manufacture of organic chemicals, and

Table 10. Removals of Organic Compounds Achieved by POTW Secondary Treatment[4]

Compound	Median Removals* (%)
BOD	91
COD	83
TOC	71
Total suspended solids	92
1,1,1-Trichloroethylene	88
Ethylbenzene	89
Methylene chloride	55
Bis (2-ethylhexyl) phthalate	60
Tetrachloroethylene	86
Toluene	94
Trichloroethylene	90

*Values obtained using data where the influent concentration was greater than 10 μg/L. This concentration was accepted as the reasonable detection level for the analytical methods that were used.

plastic and synthetic industries.[7] All of the plants used activated sludge treatment systems which included neutralization and equalization where needed, one or more aeration basins, associated primary and secondary clarifiers, and biological solids recycle systems.

All influent and effluent samples were analyzed for the organic priority pollutants, except pesticides and polychlorinated biphenyls, by gas chromatography (GC) or gas chromatography/mass spectroscopy (GC/MS) procedures. Not all organic priority pollutants were analyzed at each plant. Certain conventional and non-conventional pollutants also were measured. Data were collected over a four to six week period at each plant.

Table 11 presents data on the conventional and non-conventional pollutants collected at each plant during the period of evaluation. The information represents mean values of the collected data.

The performance of the plants, with the exception of Plant E, was good with high removals of BOD, COD, and TOC. The low performance of Plant E was attributed to the low concentration of pollutants in the influent. The BOD and TOC effluent concentrations at Plant E were comparable to those at the other plants with the BOD concentrations at each plant being less than 20 mg/L.

To preserve the confidentiality of organic priority pollutant data, the influent and effluent data from all five plants were pooled. Tables 12, 13, and 14 present the treatment plant performance data for three classes of organic priority pollutants. The data were found to be distributed in a log normal pattern and the geometric mean was used to determine the percent removal and as a measure of the "average" values. Only data based on at least five detections in the influent are presented in these tables.

With only a few exceptions, high removals of the organic priority pollutants occurred in the biological treatment systems. In addition, the effluent concentrations for most of the noted compounds were close to or below the detection limit of 10 μg/L accepted for the analytical methodologies that were used. The data also showed that generally there were fewer observations of a specific compound in the treated effluent than there were in the influent.

Table 11. Wastewater Treatment System Performance at Five Organic Chemical Industry Plants — Conventional and Non-Conventional Parameters[7]

Plant	BOD			COD			TOC		
	Influent* (mg/L)	Effluent* (mg/L)	Removal (%)	Influent* (mg/L)	Effluent* (mg/L)	Removal (%)	Influent* (mg/L)	Effluent* (mg/L)	Removal (%)
A	580	18	97	1180	153	87	378	39	90
B	450	14	97	750	95	87	—	—	—
C	840	3	99	1740	123	93	485	35	93
D	1280	19	99	—	—	—	650	60	91
E	48	14	71	—	—	—	54	23	57

*Mean values.

Table 12. Wastewater Treatment System Performance at Five Organic Chemical Industry Plants — Volatile Organic Priority Pollutants[7]

Compound	Influent* (μg/L)	Effluent* (μg/L)	Removal (%)
Acrylonitrile	10,300	65	99
Benzene	581	6	99
Bromomethane	1,250	ND	100
Bromodichloromethane	20	**	——
Chlorobenzene	20	†	——
Chloroethane	12	**	——
Chloroform	348	13	96
Dibromochloromethane	6	ND	100
1,1-dichloroethane	9	†	——
1,2-dichloroethane	524	9	98
1,1-dichloroethene	42	ND	——
t-1,2-dichloroethene	42	**	——
1,2-dichloropropane	138	7	95
1,3-dichloropropene	148	6	96
Ethylbenzene	283	†	——
Methylene Chloride	17	9	47
Tetrachloroethene	6	**	——
1,1,1-trichloroethane	7	**	——
1,1,2-trichloroethane	12	†	——
Trichloroethene	7	**	——
Toluene	4,500	7	100

*Geometric mean.
**All detections less than 10 μg/L.
†Less than five detections.

The results of this industrial wastewater study are consistent with those found in the 40 city POTW study discussed earlier, i.e., generally high organic priority pollutant removals, low effluent concentrations, and a lesser frequency of detection in the effluent samples.

The values shown in Tables 12, 13, and 14 should be used with care since they represent only geometric mean data. There was considerable variation in the data and therefore the values in the tables should be considered as illustrative rather than assuredly consistent.

In an independent study a large manufacturer of organic and inorganic chemicals sampled virtually all of its plants to determine the number and concentrations of priority pollutants in their wastewaters.[8] A total of 72 domestic manufacturing sites were sampled. The majority had wastewater treatment facilities that used biological treatment processes including nineteen activated sludge systems. Forty-two influent and 43 effluent samples were taken at these sites and analyzed for the priority pollutants.

Table 15 summarizes the concentrations of organic priority pollutants detected in the influent and effluent samples at least three times. Percent removal information cannot be calculated from these concentrations since they represent pooled data, not actual influent and effluent concentrations for a specific treatment system. A log

Table 13. Wastewater Treatment System Performance at Five Organic Chemical Industry Plants — Base/Neutral Organic Priority Pollutants[7]

Compound	Influent* (μg/L)	Effluent* (μg/L)	Removal (%)
Acenaphthene	84	**	——
Anthracene/Phenanthrene	62	6	90
Benzo(a)anthracene/Chrysene	20	8	60
Benzo(a)pyrene	13	†	——
Bis (2-ethylhexyl) phthalate	24	28	0
Di-n-butyl phthalate	86	6	93
1,2-dichlorobenzene	331	28	92
Dimethyl phthalate	46	**	——
Dioctyl phthalate	28	**	——
Fluoranthene	17	6	65
Fluorene	56	†	——
Naphthalene	802	6	99
Nitrobenzene	3,000	91	97
Pyrene	17	6	65

*Geometric mean.
**All detections less than 10 μg/L.
†Less than five detections.

Table 14. Wastewater Treatment System Performance at Five Organic Chemical Industry Plants — Acid Organic Priority Pollutants[7]

Compound	Influent* (μg/L)	Effluent* (μg/L)	Removal (%)
2-chlorophenol	53	35	34
2,4-dichlorophenol	347	24	93
2,4-dimethylphenol	270	**	——
2,4-dinitrophenol	673	59	91
2-nitrophenol	40	†	——
Pentachlorophenol	216	115	47
Phenol	171	10	94
2,4,6-trichlorophenol	100	53	47

*Geometric mean.
**All detections less than 10 μg/L.
†Less than five detections.

normal statistical distribution fit the data and the geometric mean was used as an indication of "average" values.

The data summarized in Table 15 are comparable to those presented in earlier tables. The organic priority pollutants are present in industrial wastewaters in μg/L concentrations. The geometric mean effluent concentrations are low, with most below 30 μg/L.

Table 15. Organic Priority Pollutants* in the Influent and Effluent Wastewaters of an Organic and Inorganic Chemicals Manufacturer[a]

Chemical	Influent (ug/L)		Effluent (ug/L)	
	Range	Geometric Mean	Range	Geometric Mean
Benzene	1 - 949	14.7	2 - 33	6.2
Bis (2-ethylhexyl) phthalate	1 - 500	14.2	1 - 1,400	8.5
Bromoform	6 - 10	8.1	3 - 10	6.5
Butyl benzyl phthalate	1 - 410	12.8	1 - 180	4.3
Carbon tetrachloride	1 - 1,130	19.6	1 - 20	6.3
Chlorobenzene	1 - 500	37.6	15 - 100	42.2
Chlorodibromomethane	4 - 338	20.8	2 - 15	6.3
Chloroform	1 - 7,600	21.4	1 - 500	10.3
Di-n-butyl phthalate	1 - 150	5.3	0.6 - 8	2.1
1,2-Dichlorobenzene	1 - 310	14.6	10 - 1,470	76.1
1,4-Dichlorobenzene	0.7 - 30	5.2	†	†
1,2-Dichloroethane	†	†	10 - 25	13.6
Diethyl phthalate	2 - 31	4.9	1 - 10	2.6
Dimethyl phthalate	0.2 - 130	4.8	0.8 - 92	9.6
2,4-Dinitrotoluene	†	†	1.9 - 30	8.0
Ethylbenzene	1 - 300	17.9	8 - 300	27.5
Fluoranthene	0.3 - 500	1.4	†	†
Methylene chloride	1 - 10,000	43.9	2 - 10,000	30.0
Methyl chloride	10 - 100	31.0	†	†
Naphthalene	1.2 - 17,800	94.2	†	†
4-Nitrophenol	15 - 29,200	290	4 - 374	20.8
2-Nitrophenol	16 - 8,650	258	†	†
Phenanthrene	1.7 - 30	10.6	†	†
Pyrene	0.4 - 6	2.4	†	†
Phenol	1 - 116,000	50	8 - 130	18.9
Tetrachloroethylene	1 - 200	15.1	1 - 120	8.0
1,1,1-Trichloroethane	1 - 20	6.2	1 - 40	5.9
Trichloroethylene	3 - 100	12.0	†	†
Toluene	3 - 1,000	28.9	1 - 600	20.7

*Pooled data from many facilities; compounds detected at least three times.

†Less than three detections.

Leather Tanning and Finishing

Leather tanning and finishing wastewaters contain soluble and particulate organics, dirt, and inorganics such as chlorides, sulfides, and metals. Biological treatment processes are commonly used to treat these wastewaters. These processes include activated sludge, oxidation ponds, aerated lagoons, rotating biological contactors, and trickling filters[9]. One or more of the following unit processes is part of the total treatment system in addition to a biological treatment process: grit removal, equalization, coagulation and primary sedimentation, and screening. The total treatment system can achieve high degrees of pollutant removal.

During its development of effluent guidelines and standards for this industry, EPA sampled a number of treatment facilities and analyzed their performance for conventional, nonconventional, and priority pollutants[9]. Table 16 illustrates the results that were obtained and indicates that, in general, treatment facilities that accomplish high removals of the conventional organics (BOD, COD, oil and grease) also achieve high removals of the priority pollutants.

Volatile organics measured in the influent were removed in the treatment facilities, probably due to air-stripping. A variety of metals were present and significant removals were obtained probably in the solids separation process. The actual fate of the pollutants was not determined.

Specific Organic Compounds

In addition to the evaluations noted above, there have been studies on the removal of specific organic compounds produced by industry.

In one such study, the biodegradation and toxicity of 12 organic compounds was evaluated using respirometric measurements and acclimated activated sludge tests[10]. Many of these compounds are considered potential carcinogens or toxic chemicals. The summary in Table 17 notes that many are biodegradable although, in certain cases, acclimation of the microorganisms was necessary before high removals occurred.

Summary

The available information indicates that biological treatment processes can achieve high removals of both general organic pollutant parameters, such as measured by the BOD test, and specific organic compounds. In general, when high removals of BOD, COD and other general pollutants occur in biological treatment systems, high removals of the priority pollutants also occur. There are, however, organics that are inhibitory to biological treatment systems. More information is needed on such compounds and the concentration at which they are inhibitory.

It is clear that microbial degradation is not the only mechanism of removal of organic compounds in biological treatment systems. Because of the aeration that takes place in such systems, air-stripping and volatilization as well as adsorption on suspended solids play a major role in the removal of organics.

FUTURE DEVELOPMENT AND NEEDS

General

Biological treatment is one of a variety of technologies that can treat industrial wastewaters and aid in reducing degradation of the environment. Most of these technologies are "end-of-pipe" or curative technologies. In addition, there are preventive technologies which reduce the quantity of pollutants requiring treatment

Table 16. Performance of Industrial Waste Treatment Systems Treating Leather Tanning and Finishing Wastewaters[19]*

	Biological Treatment Process											
	Separate Activated Sludge or Extended Aeration Systems									Aerated Lagoon		
	System A			System B			System C					
Pollutant	inf	eff	rem (%)	inf	eff	rem (%)	inf	eff	rem (%)	inf	eff	rem (%)
Conventional and nonconventional pollutants (mg/L)												
BOD	1240	920	26	2000	300	86	1530	49	97	1870	20	49
COD	2560	1780	31	4030	890	87	5950	550	91	5530	220	96
TSS	1100	560	49	2250	130	94	6370	340	96	2900	155	95
TKN	250	190	26	290	160	43	750	280	63	500	105	79
oil and grease	170	90	47	550	17	97	250	35	86	720	17	98
sulfide	50	30	40	16	6	63	19	17	9	200	0.4	99
Priority pollutants (µg/L)												
benzene	ND	ND	-	tr	tr	-	tr	tr	-	tr	tr	-
chloroform	41	tr	98	tr	ND	-	ND	ND	-	ND	ND	-
toluene	tr	tr	-	>100	tr	99	tr	tr	-	>100	tr	99
1,2 dichlorobenzene	215	69	68	ND	tr	-	49	ND	100	255	ND	100
1,4 dichlorobenzene	99	21	79	ND	tr	-	19	ND	100	54	ND	100
phenol	480	435	9	5500	1400	75	845	ND	100	4400	ND	100
2,4,6 trichlorophenol	10500	4300	59	ND	12	-	1700	38	98	880	ND	100
pentachlorophenol	9500	3100	67	ND	12	-	2900	200	93	ND	ND	-
bis (2-ethyhexyl) phthalate	ND	ND	-	32	6	83	ND	26	-	51	2	96
naphthalene	49	15	69	ND	2.3	-	19	ND	100	24	ND	100
phenanthrene/anthracene	56	tr	98	2.9	1.4	52	7.6	ND	100	ND	ND	-
ethylbenzene	ND	ND	-	>100	tr	99	43	tr	98	88	ND	100
chromium	31000	20000	35	170000	1700	99	6400	170	97	160000	1100	99
copper	57	37	35	220	8	96	200	25	88	50	5	90
cyanides	20	40	-	50	40	20	100	400	-	60	150	-
lead	100	30	70	3100	60	98	100	50	50	1100	80	93
nickel	5	34	-	75	30	60	60	30	50	60	30	50
zinc	230	140	39	2100	170	92	460	59	97	500	49	90

*Average results from a three-day sampling program at the noted plants.

tr - compound detected only in trace amounts, generally less than 10 ug/L.

ND - compound not detected.

Table 17. Biodegradability of Specific Organic Compounds[10]

Compound	Result
Methylethyl ketone (MEK)	—easily biodegradable, does not inhibit microbial activity up to 800 mg/L
Dimethyl amine (DMA)	—easily biodegradable at concentrations not surpassing 300 mg/L
Dimethyl formamide (DMF)	—easily biodegradable, microorganisms require acclimation before high removals occur
p-nitrophenol (PNP)	—biodegradable at concentrations up to 50 mg/L; at higher concentrations PNP is toxic; activated sludge removes PNP with high efficiency; microorganisms require acclimation
o-chlorophenol (OCP)	—biodegradable only at low concentrations, up to 10 mg/L; at concentrations up to 200 mg/L, OCP is not biodegraded but does not significantly inhibit biological processes; microbial acclimation needed
Trichlorophenol (TCP)	—biodegradable at concentrations up to 35 mg/L but needs acclimated microorganisms; 25 mg/L in activated sludge inhibits the process
2,2' dichlorodiethyl ether (DCE)	—biologically inert, no degradation even at 0.7 mg/L; a volatile compound that may be stripped during biological treatment
Fluorescent whitening agents (FWA) (used in household detergents) (five were evaluated)	—did not cause any oxygen demand but were partially decomposed in the respirometric tests, no effect on the treatability of the activated sludge units until the concentration was greater than 80 mg/L

by curative methods. Preventive technologies involve recycle and reuse of wastewaters before discharge as well as product substitution and source control to minimize unwanted pollutants in industrial wastewaters. These technologies can have a significant impact on biological treatment by reducing the toxic compounds in industrial wastewaters and the volumes of wastewaters requiring treatment.

Important innovations will occur with both preventive and curative technologies. However, while preventive technologies offer great potential for industrial pollution control, industrial wastewaters containing conventional, nonconventional, and toxic pollutants will continue to be produced and require treatment.

Developments

Current biological treatment processes will continue to be used to treat industrial wastes since they have been shown to provide excellent removal of conventional pollutants and frequently high removal of nonconventional and toxic pollutants.

Biological treatment systems have been used to remove organics that have an effect on oxygen resources of the receiving body of water. As a result, waste strength and treatment plant performance have been measured in terms of general parameters such as BOD, COD or TOC. With the increasing interest in toxic pollutants, greater attention is being paid to the removal of specific organic compounds such as the priority pollutants. This interest, plus the continuing need for treatment processes that are less energy-intensive, more reliable, and which have lower operating costs will result in improved and more innovative biological treatment processes being used in the future.

Land application of primary or secondary treated wastewaters incorporates biological treatment and offers another approach for the management of all or a part of the discharges from industry. Proper use of this treatment technology offers opportunities for nutrient recycling through crops grown on the site and for recharge and renovation of the applied wastewaters. Land application incorporates treatment with resource recovery. The movement and fate of toxic materials applied to the soil need to be more fully understood; however, preventative technologies such as pretreatment of industrial wastes and source control should minimize this problem in the future. Where land is available, greater use will be made of land application of wastes since it is less energy-intensive, less costly, and makes use of the biological, physical, and chemical treatment capabilities of the soil.

Process control of biological treatment offers considerable opportunities for development in the future. This control will result in increased reliability and more effective and consistent treatment. Better control of dissolved oxygen, nutrient addition, solids wasting, and equalization will occur. The design engineer and plant operator will have a better array of processes and methods to treat industrial wastes and achieve effluent or water quality goals.

In summary, the potential for improved and innovative preventative and curative technologies is significant. Biological treatment technologies which are more energy-efficient, are easier to control, are more reliable, and include resource conservation will see the greatest development and use.

Needs

The improved processes and systems will result only if significant gaps in knowledge are filled. The information that needs to be acquired if biological treatment processes are to be used with maximum effectiveness includes:

Mechanisms of Removal—

Insufficient information exists on the mechanisms of removal of organic pollutants, particularly potentially toxic compounds, in biological treatment systems. Although abundant information is available on the removal of conventional pollutants in a process or a system, there is only a limited understanding of whether the pollutants are removed by stripping, sorption, or degradation. Treatment plant performance data that permit input and output mass balances of pollutants in all parts of the treatment system must be obtained if we are to know how and where specific conventional and priority pollutants are removed. With such fundamental knowledge available, better treatment processes can be developed and improved system performance can be attained.

Full-scale Systems—

Much of the available information on the removal of specific organics has resulted from small-scale and relatively short-term studies. Longer term studies on large full-scale operating systems are needed to provide a better understanding of the removals of conventional, nonconventional and toxic pollutants that occur in the real world and the influence of seasonal, operational, and design factors on such removals.

Low Pollutant Concentrations—

Biological treatment processes and systems can achieve high removals of conventional and toxic pollutants. However, low concentrations of these pollutants remain in the effluent. Effluent concentrations of conventional pollutants generally are less than 20 mg/L and toxic pollutants generally are less than 100 μg/L. Both fundamental and applied studies are needed to determine how lower concentrations of these pollutants can be achieved in effluents from biological treatment processes. Information thus derived must then be applied to improve design and operation guidelines. The current approach to remove the remaining contaminants in biological treatment process effluents is to add additional treatment processes such as multimedia filtration and activated carbon after biological treatment processes. Such add-on processes increase the capital and operational costs of a treatment system and increase treatment plant operating difficulties. Improved biological treatment processes that achieve lower effluent pollutant concentrations may be more cost-effective.

Measurement—

The lack of practical monitoring and analytical techniques for toxic compounds is a critical deficiency for both municipal and industrial waste management. This deficiency impedes the specification and development of better treatment processes and the clearer definition of health related issues. Less costly analytical methods need to be developed to reduce monitoring and compliance costs and to provide greater information on the amount and type of toxics entering and discharged from industrial and municipal wastewater treatment plants. Such methods should be suitable for analysis of wastewater, sludge, soil, and the atmosphere.

Improved Processes—

Continuing emphasis on the development of improved biological treatment processes is warranted. Rather than focusing on high technology processes, research on processes that are more cost-effective, less energy intensive, and more efficient in removing potentially toxic compounds should be emphasized. These improved processes should be evaluated at a large enough scale to obtain reliable information on operating and maintenance costs.

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REMOVAL OF ORGANIC COMPOUNDS FROM INDUSTRIAL WASTEWATERS USING GRANULAR CARBON COLUMN PROCESSES

Robert P. O'Brien, Joseph L. Rizzo,
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HISTORICAL REVIEW

During the last decade, one unit process gained wide acceptance for the removal of biorefractive and toxic dissolved organic compounds. The process is adsorption, using granular activated carbon. Specifically, it is the unit process of choice for the control of many of the hazardous and toxic organics among the priority pollutants, and particularly for the removal of the chlorinated hydrocarbon pesticides.

Several innovations in the adsorption area took place during the early seventies. In May of 1970, a commercial application of the clarification/adsorption process for wastewaters was able to reduce suspended solids and oil and grease to 50 mg/L and 10 mg/L, respectively. This reduction is accomplished in conventional clarifiers with polymer addition followed by an adsorption system which removes the remaining suspended solids and dissolved organic contaminants. Prior to the announcement of this process, many studies clearly indicated that granular carbon was capable of serving the dual role of removing suspended matter and adsorbing the dissolved organics.

Dr. Walter J. Weber of the University of Michigan was carrying on some very interesting work with a unique adsorption system design[1] called the "Upflow Expanded Bed Design." In this type of system, because the granular carbon bed is expanded approximately 10%, suspended solids in the influent tend to pass through the carbon bed. Naturally, if the removal of suspended solids is an objective, another process has to be employed downstream of the carbon. Two of the largest industrial wastewater treatment plants in the United States employ the expanded bed design: American Cyanamid, in Boundbrook, New Jersey since 1978; and Mobay Chemical Company in New Martinsville, West Virginia since 1974.

In mid-1973, two companies signed contracts with Calgon Corporation for a unique adsorption service. One of these companies (Crompton Knowles)

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manufactures organic dyes, and the other (Hardwick Chemicals) produces organic chemicals. A key feature of this new adsorption system is that although the adsorption system is located at the user's plant site, the spent carbon is returned to a central reactivation center. The major benefits to industrial clients are (1) they do not have to make a major capital investment for an adsorption system, since they lease the equipment and carbon, and (2) they are relieved of any future liabilities associated with one category of waste substances. The adsorbed organics since then are completely destroyed. Furthermore, all the economies of scale can be realized with centralized reactivation facilities. Over one hundred industrial plants are now enjoying the benefits associated with the adsorption service.

In the mid-seventies, the U.S. Environmental Protection Agency (EPA) proposed effluent standards for toxic chemicals in accordance with Section 307 (a) (2) of the Federal Water Pollution Control Act. Studies by Calgon Corporation had clearly indicated that the pesticides endrin, aldrin, dieldrin, toxaphene, DDT, DDD, and DDE could be removed down to nondetectable levels.[2] Several adsorption systems including two at Rocky Mountain Arsenal in Denver, Colorado and Redstone Arsenal in Huntsville, Alabama are now in operation removing these pesticides. The majority of the 129 pollutants identified as priority pollutants by EPA are amenable to carbon adsorption. The use of adsorption as a key industrial wastewater treatment process of the future is evident.

TYPES OF ORGANICS REMOVED IN EXISTING SYSTEMS

During the 1970's, the use of granular activated carbon for dissolved organics removal in industrial wastewater evolved into an effective unit process. More than 200 adsorption systems of various sizes currently operating in the United States are removing a broad spectrum of undesirable dissolved organic compounds from wastewaters.

Review of Carbon Feasibility

Numerous studies conducted over the past ten years have shown the feasibility of using carbon adsorption in the treatment of organic chemical wastes. Some of the classes of organic compounds shown to be amenable to carbon adsorption are listed in Table 1.

These compounds are very effectively removed from water by adsorption, even in the presence of other organic compounds. In general, adsorption is favored when the contaminants: (1) have high molecular weight, (2) have limited solubility, (3) are nonpolar, and (4) contain functional groups.

Laboratory results have also demonstrated granular carbon's ability to reduce toxic compounds such as pesticides, to very low levels. Listed in Table 2 are equilibrium (isotherm) results for a number of toxic compounds. Work performed in the 1960's also showed that carbon has a great affinity for parathion and butoxy ethanol ester of 2, 4, 5 - T.

Table 3 shows some results of adsorption isotherm studies conducted over a number of years on wastewaters collected from all over the United States. The wastes are classified using Standard Industrial Classification Numbers (SIC numbers) and Table 3 reflects the major industries involved. This major survey evaluated 326 wastewaters of which 204 or 63 percent achieved greater than 90 percent removal of Total Organic Carbon (TOC) using carbon. Over 76 percent of all samples tested showed greater than 85 percent removal of TOC.

Review of Operating Systems

Because it is capable of adsorbing a broad spectrum of organic compounds, carbon is used in a wide variety of industries. Among the major industries using

Table 1. Classes of Organic Compounds Amenable To Adsorption On Activated Carbon[3]

Aromatic Solvents
Benzene, toluene, xylene

Polynuclear Aromatics
Naphthalene, biphenyls

Chlorinated Aromatics
Chlorobenzene, PCB's, aldrin, endrin, toxaphene, DDT

Phenolics
Phenol, cresol, resorcinol

High Molecular Weight Aliphatic Amines and Aromatic Amines
Aniline, toluene diamine

Surfactants
Alkyl benzene sulfonates

Soluble Organic Dyes
Methylene blue, textile dyes

Fuels
Gasoline, kerosene, oil

Chlorinated Solvents
Carbon tetrachloride, perchloroethylene

Aliphatic and Aromatic Acids
Tar acids, benzoic acids

Table 2. Equilibrium Removal Capability of Activated Carbon for Selected Toxic Compounds*[4]

		Concentration of Compound, mg/L			
Compound	pH	Before Carbon	After Carbon	% Removal	Capacity**
Aldrin	7.0	48	1.0	99+	30.0
Dieldrin	7.0	19	0.08	99+	15.0
Endrin	7.0	62	0.07	99+	100.0
DDT	7.0	41	0.15	99+	11.0
DDD	7.0	56	0.14	99+	130.0
DDE	7.0	38	1.0	99+	9.4
Toxaphene	7.0	155	1.0	99+	42.0
Arochlor 1242 (PCB)	7.0	45	0.05	99+	25.0
Arochlor 1254 (PCB)	7.0	49	0.5	99+	7.2

*Determined by standard isotherm testing procedures.
**Mg/L of the compound adsorbed per g of carbon.

Table 3. Summary of Isotherm Studies of Wastewaters from Major Industries[5]

		Number of Samples/TOC Reduction			
S.I.C. Category	Industry	>99%	85-90%	<85%	Total
2000's	Food	12	4	3	19
2200's	Textile	35	9	9	53
2600's	Paper	7	0	3	10
2800's	Chemical	103	23	51	177
2900's	Petroleum	15	1	2	18
3300's	Metal	9	1	3	13
Subtotal		181	38	71	290
% of subtotal		63%	13%	24%	100%
All other samples		23	5	8	34
Total study		204	44	76	324
% of study		63%	14%	23%	100%

granular activated carbon are those producing: plastics, textiles, dyes, agricultural chemicals, munitions, general organic chemicals, steel and pesticides. Others using carbon are refineries, chemical waste processors, ore processing and truck washing facilities.

Table 4 presents a tabulation of important design and operating parameters for carbon adsorption systems.[6] Adsorption systems are currently treating wastewaters with flows from as little as 10,000 GPD to as high as 20,000,000 GPD.

Superficial contact times vary from a low of 23 minutes to a high of 800 minutes. Carbon exhaustion rates vary, due to flow and concentration of contaminants, from a low of 55 lbs/day to a high of 120,000 lbs/day.

Treatment objectives also vary widely. In some cases they are expressed as pollutants measured in terms of such gross parameters as TOC, COD and color; in other cases, the objectives are expressed as specific chemical structures. Required effluent standards range from the mg/L range for the gross parameters to the low μg/L ranges for the specific compounds. The concentration of organics in wastewaters also varies widely, ranging from a wastewater containing as much as 15,000 mg/L TOC, in the case of one herbicide manufacturer, to as low as 10 μg/L of chlorinated organic compounds, in the case of leachate from one industrial landfill.

The wide range in influent and effluent contaminant levels reflects the flexibility of a carbon system and demonstrates that carbon is often used to supplement other forms of treatment, e.g., biological. A 1982 review of industrial systems utilizing the Calgon Adsorption Service showed that they could be classified as follows:

Carbon adsorption only	43 percent
Carbon adsorption preceding biological treatment	24 percent
Carbon adsorption combined with biological treatment	7 percent
Carbon adsorption only, with reuse	10 percent
Carbon adsorption with other treatment/disposal process	16 percent

Carbon adsorptions systems preceding biological treatment are generally used to remove compounds which are toxic to the micro-organisms. In cases where the biological treatment is utilized ahead of the adsorption system, the carbon is added because biological treatment alone cannot meet the treatment objective.

Table 4. Review of Operating Adsorption System Parameters

Client Plant	Flow (GPD × 10^3)	Pretreatment*	System Design	Superficial Contact Time (Minutes)	Types of Organics In Wastewaters	Treatment Objective	Influent (mg/L)	Effluent (mg/L)	Carbon Exhaustion Rate (lbs/day)
Landfill Leachate	24	N	2 Stage 1 Train	628	Hexachloroethane Hexachlorobutadiene Hexachlorobenzene	Hexachlorinated Organics	10 μg/L	non-detect	223
Landfill Leachate	10	E C F							
Specialty Chemicals	200	P C F	2 Stage 1 Train	40	—	TOC Removal	30	4	55
Specialty Organics	40	P E	2 Stage 1 Train	200	—	TOC Removal	4000	750	438
Herbicide Manufacturing	144	P E	2 Stage 1 Train	48	Phenol	TOC Removal Phenol Removal	1650 250	20 <1	2250
Resin Manufacturing	36	E P	1 Stage 1 Train	193	—	Phenol Removal TOC Removal	275 400	<0.1 <20	274
Specialty Chemicals	500	B S F	2 Stage 2 Train	32	Phenol	Phenol Removal	20	5	5300
Engine Repair	200	L F	2 Stage 1 Train	78	Alkanes, Phenol Dioctyl azelate	Phenol Removal	30	<0.1	1440
Landfill Leachate	30	P	2 Stage 1 Train	40	Chloroform Carbon Tetrachloride Trichloroethylene Perchloroethylene	Chlorinated Hydrocarbon Removal	50	0.001	700

Coke Manufacturer	255	C F	2 Stage 2 Train	135	Phenol Methyl ethyl ketone	Phenol Removal	150	1	6250
Resin Manufacturer	200	E	2 Stage 2 Train	78	Alkyl phenol	Phenol Removal	150	<0.1	6000
Specialty Manufacturers	220	E	2 Stage 1 Train	64	Methylene Chloride Chloroform Toluene Benzene Carbon Tetrachloride	COD Removal	200	20	3300
Pesticide Manufacturing	144	E O F	2 Stage 1 Train	55	Methylene Chloride	Pesticide Removal	125	0.1	700
Pesticide Manufacturing	86	E F	2 Stage 1 Train	90	—	Pesticide Removal	1-2	0.1	1200
Plastic Manufacturing	350	B F	2 Stage 1 Train	23	Phenolics	Phenol Removal	0.5	<0.1	1600
Specialty Chemicals	10	E	2 Stage 1 Train	800	MBAS, Phenol, O-Cresol, Ethers	TOC Removal	3600	60	700
Chemical Washing & Waste Processing	200	E F	2 Stage 1 Train	40	Phenols Xylene, Alkyl Benzene Benzaldehyde,	Phenol Removal	80	<0.1	525
Pesticide Manufacturing	250	E C	2 Stage 1 Train	32	Atrazine	Atrazine SOC	35 45 3500	<0.1 <0.002 16	2700
Specialty Resins	50	O E F	2 Stage 1 Train	160	Phenol, Naphthalene, Diethyl phthalate, Methylene Chloride	Phenol Removal	40	0.5	4900
Herbicide Manufacturing	43	E	2 Stage 1 Train	191	—	TOC Removal	600	60	1370

Table 4. (Continued).

Microbiocide Manufacturing	50	E	2 Stage 1 Train	138	Dimethylamine	TOC Removal	1500	2	2100
Specialty Chemicals	43	E F	2 Stage 1 Train	350	Toluene diamine	COD Removal	480	50	330
Specialty Chemicals	500	F	1 Stage 2 Train	32	Benzene Toluene Phenol Naphthalene	Naphthalene Removal	10	<0.1	550
Synthetic Textile Manufacturing	115	N	1 Stage 1 Train	55	—	Color Removal	—	—	275
Waste Processing	60	S F P	2 Stage 1 Train	175	Various Hydrocarbons	TOC	52	<20	2300
Ore Processing	80	E P	2 Stage 1 Train	100	—	Surfactant Removal	225	<75	329
Dye Manufacturing	150 P	E P	2 Stage 1 Train	55	Organic Dyes	Color Removal (APHA)	1300	<150	4000
Pesticide Manufacturing	170	E P	2 Stage 1 Train	40	—	TOC Removal	600	20	8700
Specialty Chemicals	150	P	2 Stage 1 Train	46	Benzene Aniline 180 mg/L Dinitrophenol 480 mg/L Nitrobenzene 1300 mg/L	Benzene Removal	280	<2	4500
Herbicide Manufacturing	23	P	2 Stage 1 Train	400	Phenylenediamine Methylester	TOC Removal	15,000	2000	19,000
Synthetic Fibers Manufacturing	120	E	2 Stage 1 Train	75	Dimethylamine Chloroform	Solvent Removal	120	<0.01	3300

Table 4. (Continued).

Organic Intermediates	20	E F	2 Stage 1 Train	400	Chloroform	TOC Removal	6400	1600	10,000
Herbicide Manufacturing	300	S F	2 Stage 2 Train	55	Phenol Xylene Triethylamine Nitrophenol Chloronitrobenzene	TOC Removal Phenol Removal	1300	<600 <0.01	8400
Specialty Chemicals	35	E P O	2 Stage 1 Train	199	2-MIN Dimethyl Sulfate	Odor Removal	—	—	219
Naval Stores	1080	C B	Parallel Moving Beds	—	—	TOC	—	—	22,000
Organic Chemicals	1950	E B	Parallel Moving Beds	—	Toluene diamine	TOC	—	—	11,000
Organic Chemicals	504	E P L	Parallel Moving Beds	—	Phenol Urea	TOC	—	—	30,000
Organic Chemicals	20,000	E C A F	Parallel Moving Beds	30	Dyes, Pigments, Various Chemicals	TOC	—	—	120,000
General Chemicals	15	E	1 Train 3 Stage	540	Xylene	TOC COD	6400 28,500	400 1300	6500

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*Abbreviations as follows: N=none; E=equalization; C=clarification; F=filtration; P=pH adjustment (control); B=biological; S=settling; L=sedimentation; O=oil and grease removal; A=aeration

PRETREATMENT REQUIREMENTS FOR ADSORPTION SYSTEMS

The pretreatment process or processes required will be dictated by the adsorption system design employed and the wastewater constituents. This section discusses the types of pretreatment processes utilized with the various adsorption system designs.

Conditions Requiring Pretreatment

Industrial wastewaters may contain many types of contaminants which interfere with, and reduce the effectiveness of, the adsorption process, indicating that pretreatment should be considered. Suspended solids, insoluble or free oils and grease, and chemically unstable wastewaters could be particularly troublesome.

The objective of the suspended solids removal process is to prevent a premature excessive pressure drop through the carbon bed. The maximum desirable concentration of suspended solids that a backwashable adsorption system can treat economically is approximately 50 mg/L to 65 mg/L at a hydraulic loading of 4 gpm/ft^2. At this suspended solids loading, one backwash using approximately 2.5% of the total process water will be required for each 24-hour operating period. Obviously, higher concentrations of suspended solids or higher hydraulic loadings will require more frequent backwashing. Normally, the backwash water is returned to the head of the plant. If the clarifier is operating at capacity, a backwash water collection tank may be employed to permit control of the rate at which the suspended-solids-laden backwash water is returned to the system. It should be noted that the suspended solids in the backwash water settle more rapidly than do the solids in the wastewater entering the treatment plant initially. Where necessary, conventional clarifiers, with and without polymer addition, have been utilized to reduce the suspended solids concentration. If the suspended solids float, air flotation units have been successfully used to achieve reduction. High-rate pressure filters using sand or mixed media also have been successfully employed.

Insoluble oil and grease in the influent to a carbon adsorption system can coat the granular activated carbon and cause loss of adsorption capacity. Skimmers in the clarifiers and air flotation units have been successfully used to reduce the levels of these contaminants to the maximum desirable concentration of approximately 10 mg/L. Concentrations of insoluble grease and oil as high as 50 mg/L have been successfully treated in adsorption systems. In these systems, the oils and grease are removed in the upper portion of the carbon bed which, as a consequence, loses its adsorptive capacity and must be sacrificed.

High concentrations of calcium carbonate or calcium sulfate in wastewater coat the granular activated carbon and cause a loss of adsorptive capacity. Such carbon may have to be discarded because it cannot be reactivated. The objective of pretreatment in such a case is to increase the wastewater stability. This can be accomplished by simple pH adjustment or the addition of a scale-inhibitor such as sodium hexametaphosphate.

Four types of adsorption systems have been employed in industry for wastewater treatment, each imposing different requirements on pretreatment processes. The system using fixed downflow beds in parallel operation is flexible, since backwash capability may be designed into the system. This capability may include air scour or surface washers to break up the solids which collect on the top of the carbon bed. Experience indicates an adsorption system having backwash capability can handle the aforementioned 50 mg/L to 65 mg/L suspended solids at a hydraulic loading of 4 gpm/ft^2 on a continuous basis when being backwashed once every 24 hours.

Backwashing capability may also be designed into the adsorption system using downflow beds in series; the parameters used for the fixed-bed parallel system are applicable here, too. However, if backwash is not included, experience indicates the system influent should contain no greater than 10 mg/L of suspended solids. The first bed in the series will collect the solids and must be designed to be taken off stream for reactivation prior to being limited by a high pressure drop.

The adsorption system consisting of upflow-packed fixed beds in series has virtually no capacity for handling suspended solids. If a premature high pressure drop occurs, the entire carbon bed must be removed. In this case pretreatment to reduce the solids to approximately 5 mg/L to 10 mg/L is essential.

The adsorption system employing upflow expanded beds permits the suspended solids to pass through the granular activated carbon. This occurs because the granular carbon bed is expanded approximately 10 percent. If suspended solids removal is an objective, it must be accomplished by a final solids removal process.

KEY DESIGN PARAMETERS

The design of an efficient and economical adsorption system for treating wastewater should be approached in the same manner as the design of any unit process in a chemical plant. Careful planning and testing are essential in order to generate the firm data on which design decisions must be based. The sequence of steps needed to provide the data required to design a carbon adsorption system has been detailed by Hansen and Froelich[7] and Rizzo and Shepherd.[8]

Wastewater Survey

The first and most important step in solving an industrial wastewater treatment problem is to conduct a thorough wastewater survey, which includes analysis of flows and of the quantity and types of pollutants at key points in the wastewater system. The three basic objectives of a wastewater survey are: (1) thorough characterization of the constituents present, (2) definition of conditions representing problems in use of activated carbon treatment, or favoring treatment processes other than adsorption and (3) assistance in the wastewater process design. The wastewater survey may improve the quality of the feasibility study design, or it may actually aid in determining the most effective point at which to apply adsorption and thus assure a more economical use of the carbon.

Analytical tests outlined by Hansen and Froelich[7] permit a reliable general characterization of a wastewater when considering treatment by activated carbon. This should include determination of total and soluble organic carbon, and total and soluble chemical oxygen demand which indicate the nature and quantity of organics present in the wastewater. The presence of inorganic components including calcium, sodium, chlorides, phosphates and sulfides suggests potential problems in the reactivation process such as air pollution, slagging or corrosion. Measurement of pH, suspended solids, immiscible oils and grease, and chemical stability are needed in determining whether pretreatment or post-treatment to activated carbon is necessary. More specific analyses should be conducted when toxic and refractory organics are present. In this case, sophisticated testing is required, since chemicals of interest may be present in very low concentrations. A reliable characterization of such compounds can usually be obtained by gas chromatograph/mass spectrophotometry.

Evaluating Adsorption Feasibility

The first step in assessing the feasibility of granular activated carbon treatment for a specific application is development of a liquid-phase adsorption isotherm in the laboratory. Data for isotherms are obtained by treating fixed volumes of the contaminated wastewater with a series of known weights of carbon. The carbon-wastewater mixture is agitated at a constant temperature for one to three hours. After the carbon and the wastewater reach adsorptive equilibrium, the carbon is removed and the residual contamination in the wastewater is measured by an appropriate analytical method. Specific information on how to construct isotherms and interpret the data from single component isotherms is provided in a number of references, including the article by Hansen and Froelich.[7]

The isotherm plots of mixed-solute wastewaters commonly found in industry are frequently nonlinear and more complex to interpret. Such plots may exhibit a series of straight lines with dissimilar slopes, each representing one of the components in the mixture. In such cases, each of the lines can be treated as a separate isotherm and a theoretical carbon demand can be calculated by summing the weights required for removing each contaminant. An example of such an isotherm is presented in Fig. 1.

In general, isotherm studies can provide the following information:

1. the attainable effluent after granular carbon treatment
2. the equilibrium adsorption capacity of the carbon (maximum weight pickup of organics)
3. the optimum pH for adsorption
4. the effect of concentration of the contaminants on the adsorption capacity
5. the effect of competitive adsorption on capacity

This information is invaluable for making a quick determination of the feasibility and economic viability of granular carbon treatment. However, additional information from pilot column studies is needed before the detailed design of a carbon treatment system can be optimized.

Dynamic Column Testing

Assuming isotherm tests prove that granular carbon adsorption is capable of producing an effluent of suitable quality and that the theoretical carbon usage is economically acceptable, one may then proceed to determine the full-scale adsorption system design parameters. Of primary importance are the determinations of the optimum operating capacity and contact time which are needed to establish the column dimensions and the number of units needed for continuous treatment. Optimum contact time depends upon the rate at which the contaminant is adsorbed by the carbon and can be determined by dynamic pilot column testing.

The test is usually conducted with a series of columns containing carbon. The superficial contact time usually is in the range of 60 to 150 minutes but can be greater. A typical pilot-column arrangement is shown in Fig. 2.

Wastewater is pumped through the column system, and effluent samples are collected at appropriate intervals from each of the columns. The amount of impurity remaining in the samples is plotted as a function of volume throughput for each column. The result is a series of curves that vary in shape, depending on the dynamics of the system.

The point at which the impurity in a column effluent exceeds the treatment objective is called the breakpoint. That part of the curve between the initial leakage and the point where the column effluent concentration is the same as the influent is called the breakthrough curve (Fig. 3).

During adsorption, the carbon in the inlet section of a column becomes saturated with impurities, whereas the carbon in the outlet section remains relatively virgin. Between these two extremes lies the adsorption zone, where the removal of impurity is actually taking place. As the carbon becomes saturated, the adsorption zone moves through the bed. The time required for appearance of the breakpoint in the effluent, as well as the slopes of the breakthrough curves, provides an index of the relative depth of the adsorption zone.

From the breakthrough curve, the volume of acceptable effluent collected for each contact time can be read directly. From isotherm curves, the minimum carbon exhaustion rate (pounds of carbon used per unit volume of wastewater treated) can also be calculated. With these data, one can plot a curve of contact time vs.

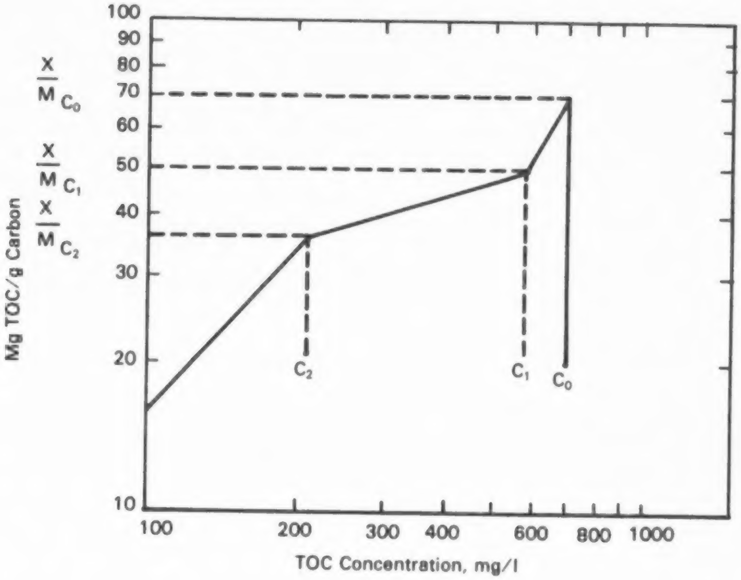

Figure 1. Isotherm plot of wastewater containing multi-components.

The carbon usage rate is determined by using the following equation:

$$\text{LBS/1000 gal.} = \left[\frac{C_0 - C_1}{\frac{X}{M_{C_0}}}\right] + \left[\frac{C_1 - C_2}{\frac{X}{M_{C_1}}} + \ldots\right] \times 8.337$$

From Figure 1 obtain the following values:

$C_0 = 700$ mg/L $\qquad \frac{X}{M_{C_0}} = 70$ mg/g

$C_1 = 575$ mg/L $\qquad \frac{X}{M_{C_1}} = 49$ mg/g

$C_2 = 220$ mg/L $\qquad \underline{X} = 36$ mg/g

Substituting these values into the equation gives:

$$\text{LBS/1000 gal.} = \left[\frac{700 - 575}{70} + \frac{575 - 200}{49} + \frac{{}^{*}220}{36}\right] \times 8.337$$

$$\text{Theoretical Carbon Usage} = [15.14] \times 8.337 = 126 \text{ lbs/1000 gal.}$$

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*Example assumes 100% removal of TOC.

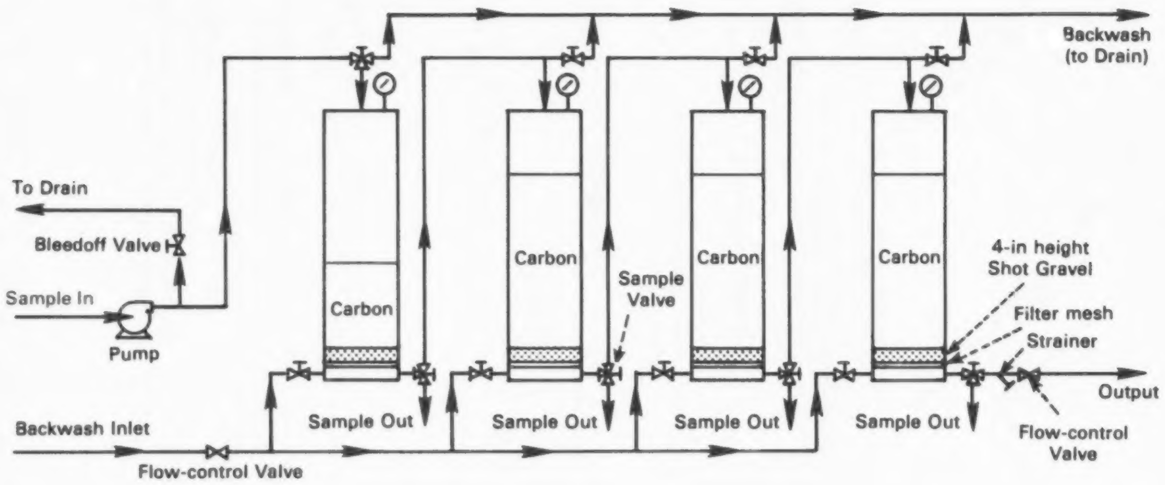
Backwash
(to Drain)
To Drain
Bleedoff Valve
Sample In
Pump
Carbon
Carbon
Carbon
Carbon
Sample Valve
4-in height
Shot Gravel
Filter mesh
Strainer
Output
Backwash Inlet
Flow-control Valve
Sample Out
Sample Out
Sample Out
Sample Out
Flow-control
Valve

Figure 2. Pilot system flow diagram for evaluating the feasibility of carbon adsorption.

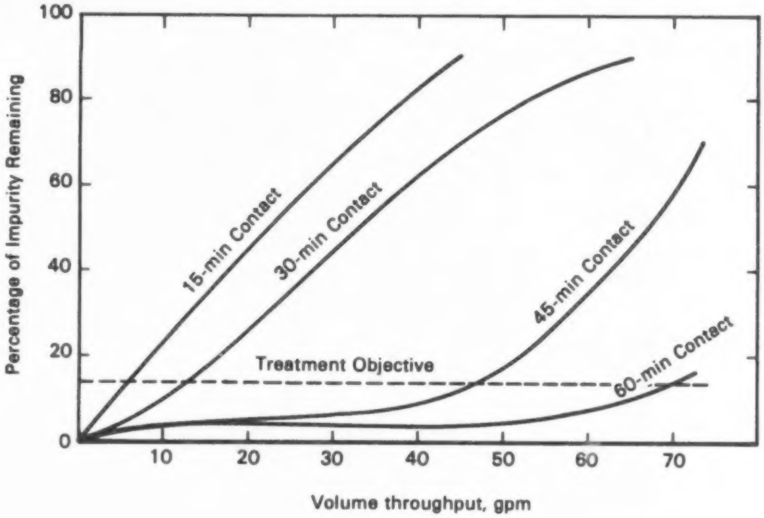

Figure 3. Typical breakthrough curves from pilot carbon adsorbers.

exhaustion rate (Fig. 4).[9] Such a curve reveals at a glance whether there is anything to be gained from long contact times. At the point where the curve becomes asymptotic to the minimum carbon usage line, there is no advantage in increasing adsorber volume to extend contact time.

Depending upon the type of full-scale adsorber system contemplated, further pilot test work may be necessary. Hansen and Froelich provided procedures for evaluating the operation of fixed beds in series.[7]

Reactivation Testing

Economics favor the use of granular carbon because it can usually be reactivated and reused. It is, therefore, important to confirm that the spent carbon generated in the column test can be successfully reactivated.

Tests need to be conducted to determine the quality of reactivated carbon which can be obtained and the degree of difficulty in reactivating the carbon. The difficulty of reactivation is an important parameter in sizing a furnace.

Tests also need to be conducted to determine the possible emissions generated during reactivation and to determine the corrositivity of the spent carbon. These parameters are necessary in order to design air pollution control devices for the reactivation system and to select the proper materials of construction.

DESIGN OPTIONS

After it has been decided that adsorption on activated carbon is the applicable technology, the following questions must be answered: (1) Should powdered or granular activated carbon be used? (2) Should/can the carbon be regenerated on-site? If not, should it be regenerated off-site? (3) What type of adsorption system should be used?

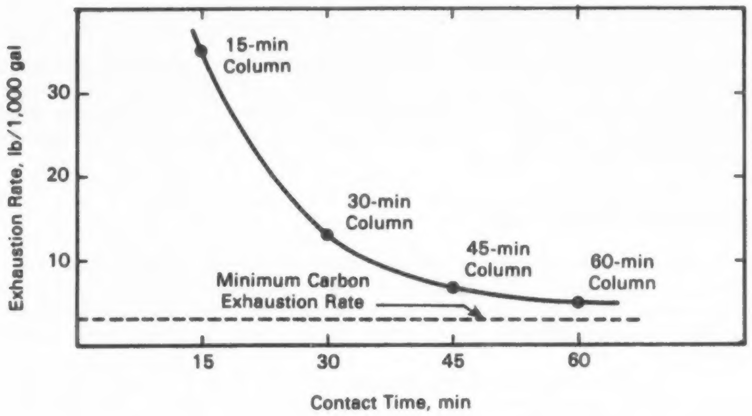

Figure 4. Superficial contact time vs. exhaustion rate.

Granular or Powdered Carbon

Selection of the form of carbon to be used is based on an assessment of various factors, particularly control of effluent quality, system efficiency, and required capital investment.

In all powdered-carbon systems, there are times when the effluent contains excessive concentrations of organic substances. This occurs because the carbon dosage is determined on an "average" influent quality. If there is a sudden surge in soluble organics due to unforeseen spills and leaks, the average carbon dosage may be insufficient to remove the excess organics. This may be especially troublesome in plants which employ batch operations. Because these usually produce wide variations in types and concentrations of organics, it is almost impossible to preanalyze the expected waste and adjust the carbon dosage accordingly.

On the other hand, a granular carbon system is capable of successfully treating wide variations in concentration of organic substances, pH and flow because there is always a combination of fresh (virgin or regenerated) and partially spent carbon on-stream. In fact, a granular system can be designed and operated to insure that the contaminant level in the effluent is always below the maximum allowable concentration.

When powdered carbon is used in a single-batch treatment system, its adsorption capacity is not fully utilized. Therefore, the designer sometimes exercises the option to use the carbon in two or three batch steps in an attempt to approach a countercurrent-type operation. However, the designer can provide a granular carbon system which is designed to provide the advantages of countercurrent operation. This type of system effectively utilizes all of the adsorption capacity of the carbon and thus the carbon usage per gallon of water treated is lower.

Often with only minor capital outlay, addition of new equipment or modifications to existing equipment will permit the use of powdered carbon. Additional costs can be incurred, however, if it is necessary to provide storage space for the powdered carbon.

In order to utilize granular carbon it is usually necessary to invest some capital. Amounts will vary significantly depending upon (1) whether or not existing filters can be used, as is often the case in potable water plants, and (2) whether the carbon is to be thrown away, regenerated on-site or off-site, or leased and regenerated off-site.

On-Site Vs. Off-Site Regeneration

If carbon is to be regenerated several factors determine whether regeneration should be done on-site or off-site: (1) availability of capital, (2) availability of space, (3) availability of people, (4) capital investment for types of processing operations required on-site, (5) local air and water pollution guidelines, and (6) possible recovery and reuse of organics.

Adsorption System Type

When the system designer has chosen the form of carbon and the type of ion carbon regeneration, he still must select the type of adsorption system which will provide a quality effluent most reliably and economically. This discussion is limited to those systems using granular carbon since these generally offer greater advantages.

Currently, there are two basic types of adsorbers which can be designed to operate under pressure or at atmospheric pressure. These are commonly referred to as moving or pulse-bed and fixed-bed. Each can be operated as either packed or upflow expanded beds.

In the pulse-bed adsorber, the liquid enters the bottom cone and leaves by way of the top cone. Periodically, when the maximum effluent criterion in terms of, say, TOC is reached, the flow of liquid is stopped. Spent carbon is withdrawn (pulsed) from the bottom and virgin or reactivated carbon enters the top.

In a fixed-bed adsorber, the liquid passes through the carbon until the carbon is spent or the maximum effluent criteria is reached. At that point, the entire volume of carbon is removed and replaced by virgin or reactivated carbon.

The choice of system depends on many factors. One which has not been widely appreciated is the variation in the effluent quality in the two types of adsorbers. The concentration of organics in the effluent from the system will have the greatest fluctuation in a single fixed-bed system. A typical profile of effluent concentration variation is depicted in Fig. 5. In this case the carbon in the adsorber must be changed each time the effluent reaches the maximum specified level of impurity. Thus, the average quality of the effluent is significantly better than the specification value. There would be an obvious advantage here in operating several columns in parallel and blending the effluents.

Since a pulse-bed system is generally operated so that less than 10% of the carbon is pulsed at any one time, the variation in the effluent is much less than that of the fixed-bed system. A profile is shown in Fig. 6.

It will be noted that the average effluent concentration is maintained close to the maximum specification value. This type of operation results in a lower carbon dosage. The magnitude of this variation can be changed by varying the size of and/or frequency of the pulse.

In a well designed continuous countercurrent system the effluent quality would be constant as shown in Fig. 7. As of now there are none of these in operation.

Some of the advantages and disadvantages of each system are given below:

Fixed-Bed System (Non-Expanded)—

Advantages

- Has lowest building profile
- Requires least operator attention
- Has less carbon fines in the effluent
- Lends itself to on-site regeneration of carbon
- Can be inspected internally as often as the adsorber is emptied
- Can treat water containing up to 50 mg/L suspended solids
- Can be backwashed and air scoured
- Requires lower inlet water pressure to pass through the system

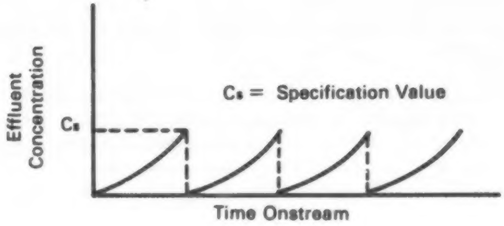

Figure 5. Effluent quality vs. adsorber changeover.

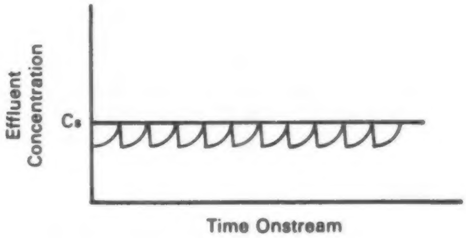

Figure 6. Effluent quality vs. pulse frequency.

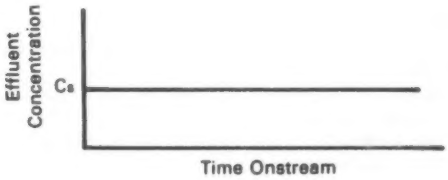

Figure 7. Effluent quality in continuous countercurrent system.

Disadvantages

- Requires the greatest amount of plot area
- Has higher capital investment
- Effluent quality can, in many cases, vary from no adsorbate in the effluent, when a fresh adsorber is placed on-stream, to specification value when a spent adsorber is taken off-stream.

Pulse-Bed System (Non-Expanded)—

Advantages

- Requires least plot area. This is probably the most important consideration when putting a system into an existing plant.
- Can be controlled to have the effluent quality close to the specification value as

shown in Fig. 6.

- Has lowest carbon dosage in applications having a long adsorption mass transfer zone.

Disadvantages

- Cannot treat liquids containing >5 mg/L of suspended solids
- Adsorber is not emptied in normal operation; therefore, inspection and/or repairs can only be done by taking an adsorber off-line and emptying the entire contents of carbon into temporary containers.
- Effluent usually contains carbon fines after each pulsing operation

Up-Flow Expanded Bed

Both fixed-bed and pulse-bed systems can be operated in the up-flow expanded mode. This mode of operation permits the suspended solids in the influent to pass through the carbon bed. To assure that this will occur, the designer must provide a pilot column utilizing the actual wastewaters operated at the expected flow conditions. In addition, the type of liquid distribution system proposed for use in the fixed-bed system should be tested to insure that plugging will not occur. Utilizing backwashing to expand the bed and remove solids defeats the purpose of this type of adsorber since the carbon particles will be redistributed, thus destroying the mass transfer zone. Also, carbon losses are higher in this type of system.

System Configuration

Each of the two types of adsorbers can be arranged in various ways. Those shown in Fig. 8 are: (1) single adsorber, (2) two or more adsorbers in series, (3) two or more adsorbers in parallel, and (4) four or more adsorbers in series - parallel.

Selection of a particular system is generally based on the following factors:

Fixed Bed—

Single Adsorber

- Mass transfer zone is short, i.e., saturation of the carbon occurs shortly after breakthrough.
- Carbon dosage is low and the cost of replacing or reactivating the carbon is a minor operating expense.
- The investment required for a multiple column system cannot be justified by the resultant lower carbon dosage.

Two or More Beds in Series

- The performance is such that saturation of the carbon occurs a long time after breakthrough, i.e., the mass transfer zone is long.
- Influent concentration fluctuates widely.
- It is economically attractive to have more stages in order to more completely exhaust the carbon.

Two or More Beds in Parallel

- The flow rate is high and the size of the adsorbers in a single pass would be too large to be economical or feasible.
- It is necessary to operate with a minimum pressure drop.
- Average effluent quality is desired to be essentially equal to specification value. This is achieved through blending of the effluents from the adsorbers.
- Space limitations prevent the use of large diameter or extremely high vessels.
- The adsorption process must be continuous.

Two or More Beds in Parallel - Series

- Flow rate is high.
- It is desirable to have a lower carbon dosage than is possible with parallel only operation.

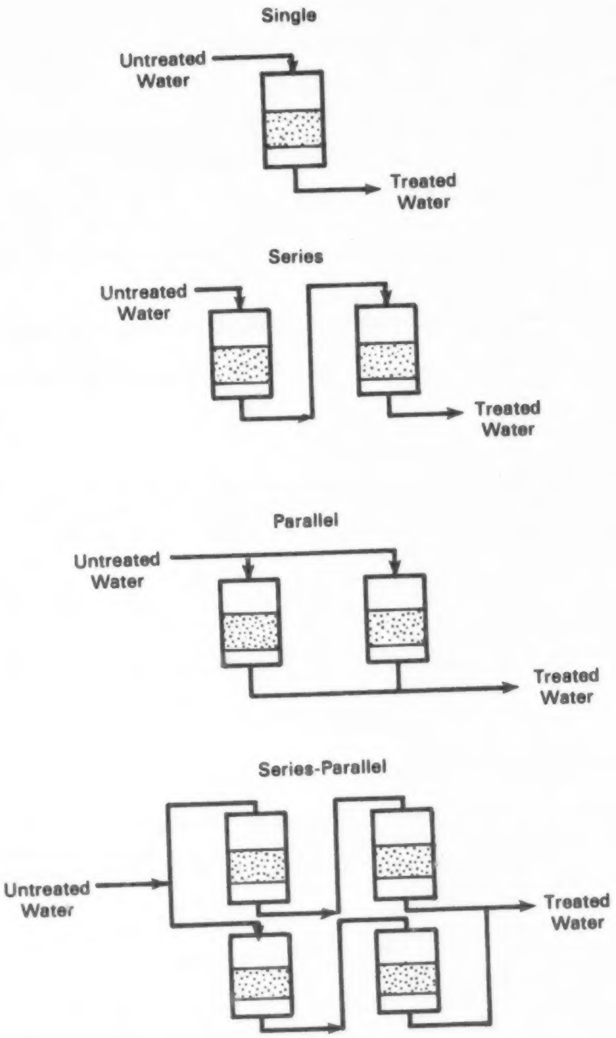
Single
Untreated Water
Treated Water
Series
Untreated Water
Treated Water
Parallel
Untreated Water
Treated Water
Series-Parallel
Untreated Water
Treated Water

Figure 8. Fixed bed system configurations.

Pulse Bed—

- The mass transfer zone is extremely long and there is an incentive for obtaining the minimum carbon dosage.
- Suspended solids are <5 mg/L.
- Minimum capital investment is desired.
- There is a desire to minimize wide fluctuations in the effluent.

Selection of Type of Fixed Bed—

If fixed beds are selected, a choice must be made between two modes of operation, i.e., pressure or atmospheric.

The advantages of the pressure vessel are:

- Carbon removal can be fairly easy.
- Allowable pressure drop due to suspended solids is limited only by design pressure of adsorber and frequency of backwashing.
- Installation is above grade.
- Operation in series is easily accomplished.
- Selection of type of material is not limited.

Atmospheric open-type adsorbers are used under the following conditions:

- Available pressure is determined by gravity only.
- There are many beds in parallel.
- Pressure build-up due to solids will be less than 5 psi per 24 hours.
- Flows are high.
- Concrete or lined concrete is a suitable material of construction.

REGENERATION

If the carbon must be regenerated to assure an economical carbon process, the following regeneration techniques may be considered: steam regeneration, chemical regeneration and thermal regeneration. Usually steam regeneration is used when the adsorbed organic compound(s) has a boiling point less than 150°F and/or when it has a reuse value which makes this technique economical; however, few applications are known. Likewise, chemical regeneration is a limited technique and is infrequently used, although caustic has been used to regenerate carbon which has been used to treat wastewater containing phenol. In the latter case the sodium phenolate which is formed is reused in the process. The most widely used regeneration technique is thermal reactivation, for which two basic process modes generally are used: direct fired and indirect fired.[10]

Types of Equipment for Thermal Reactivation

The following types of equipment currently are being employed for thermal reactivation of carbon which has been used to treat industrial wastewater (presented in order of on-stream carbon reactivation capacity and number of operating units):

- Multiple Hearth Furnace
- Vertical Tube-Type Furnace
- Direct Fired Rotary Kiln
- Fluidized Bed
- Indirect Fired Rotary Kiln
- Infrared Furnace (Indirect Heating)

The multiple hearth furnace is the most widely used for thermal reactivation; its advantages and disadvantages and those of rotary kilns have been widely reported.[11]

The fluidized-bed furnace and infrared furnace have only recently been applied to reactivating granular carbon used in treating industrial wastewater. Experience to be obtained in the next few years will determine whether or not these types of equipment will have a significant role in future carbon reactivation, particularly when the adsorbate on the carbon causes corrosion and formation of slag, and is difficult to remove in the reactivation process.

Environmental Considerations

Thermal reactivation of carbon which has adsorbed impurities from industrial wastewaters conceivably may present health hazards. These may be adequately controlled with properly designed equipment. Wet or dry scrubbers are used to remove components such as SO_2, HF and HCl from the exhaust gases. The scrubbers are also effective in removing carbon fines and ash components.

Organic compounds which are volatilized in the furnace can be oxidized to CO_2 and H_2O in a direct fired afterburner which operates at temperatures of 1400-2000° F and contact times of one to two seconds.

Energy Considerations

An important factor in selecting the type of equipment is its energy requirement and that of an ancillary afterburner and/or scrubber. Since the capital and operating costs of these units are related to the volume of gases being treated, the selection of direct or indirect heating systems has a major impact on costs. The advantages are all in favor of indirect systems. The volume of gases from an indirect system is only 25% of that from a direct fired system, and the fuel consumption in the afterburner is reduced 75%. Because the volume of gases is less, the size of the induced draft fan, ducting, scrubber and stack are smaller with subsequent savings in capital and operating costs.

Additional savings are obtained because of the elimination of steam addition. In the indirect units, carbon and evolved gases can flow concurrently. Thus, instead of having to add steam to serve as the oxidizing gas in the high temperature zone of the furnace, the water which is evaporated from the pores of the carbon in the inlet portion of the furnace serves this function.

CAPITAL AND OPERATING COST ESTIMATES

Since a carbon system consists of adsorption and, in some cases, carbon reactivation equipment, the costs are presented separately for the two systems. Also, since a small adsorption system can have a large reactivation system or a large system can have a small reactivation system, combining the costs is not meaningful.

Adsorption System Costs

The capital costs shown in Fig. 9, have been estimated for fixed-bed adsorbers with and without backwash and air scouring.

The design basis is as follows:

Flow, MGD	0.5 - 3.0
Surface Loading, gpm/ft^2	3
Superficial Contact Time, hr.	1
No. of Adsorbers in Series	2
Backwash Rate, gpm/ft^2	12 - 15

The cost includes site preparation, foundations, building, feed and backwash pumps, air compressor, electrical, automatic controls, engineering, overhead and profit. It is assumed that all utilities and off-site facilities are available at the battery limits of the system.

The operating costs associated with the adsorption process are minor. The only utility which is required is power Based on 4¢/KWH, the dollar costs per day are 16, 32 and 64 for flows of 0.5, 1.0, and 2.0 MGD, respectively. Operator attention for this type of system is minimal, i.e., periodic checks two or three times per shift is normally all that is required.

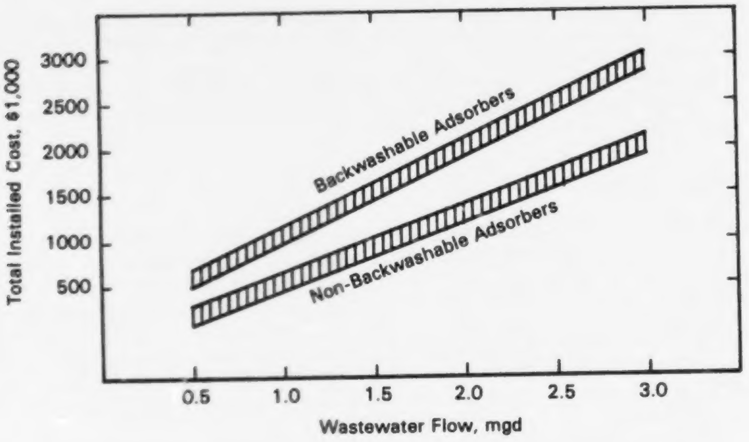

Figure 9. Installed costs for fixed bed adsorption systems.

Reactivation System Costs

The total installed costs shown in Fig. 10, are based on using multiple hearth furnaces or rotary kilns. The basis for developing the installed costs is that used for the adsorption process. The design basis is as follows:

- Furnace size based on 80 lb/Day/ft^2 of hearth area
- Afterburner and water scrubber is included
- Spent and Reactivation Storage Tanks, 40-80,000# of carbon capacity
- Operating costs for reactivating spent granular carbon are shown in Table 5. The basis for the costs is as follows:
- One operator per shift at $16/hr, plus 25% for supervision
- Fuel for furnace and afterburner - 8,000 BTU/lb carbon at $4/million BTU
- Steam rate of 0.6 lb/lb carbon at $5/1,000 lb
- Power at 4¢/KWH
- Makeup carbon - 7% of the reactivation rate @ 80¢/lb
- Maintenance @ 8% of installed costs
- General plant overhead for insurance, taxes, monitoring, accounting and administrative
- Onstream time - 330 days/year

ENERGY REQUIREMENTS

Because of the growing scarcity and the rising cost of fuels, energy requirements represent a major factor in the selection of wastewater treatment processes. A review of the energy requirements for an adsorption system and for a conventional biological system was made by Bernardin & Petura.[12] They compared the energy requirements for a 1 MGD, one stage completely-mixed activated sludge system requiring 20 hours aeration with clarification, sludge thickening, vacuum filtration and incineration with the requirements for a 1 MGD activated carbon system consisting of collection sump, pump, one pulsed granular activated carbon adsorption bed and a 5,000 lb/day reactivation facility. It was assumed both systems could handle the same influent (200 mg/L TOC) and produce the same effluent (20

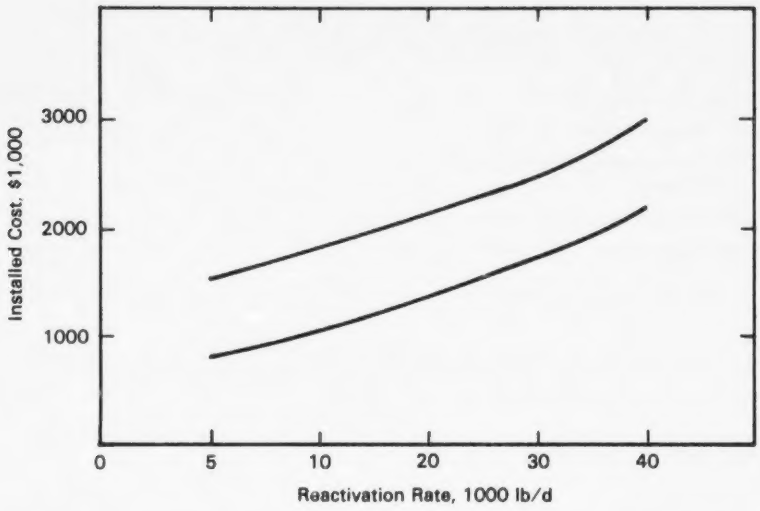

Figure 10. Installed costs for reactivation systems.

Table 5. Operating Costs ($1,000/yr) For Reactivating Spent Granular Carbon

	Reactivation Rate, lb/Day			
	5,000	10,000	30,000	60,000
Fuel	55	110	320	640
Power	15	30	75	105
Steam	5	10	30	60
Makeup carbon	90	180	540	1,080
Maintenance	90	100	150	200
Labor and supervision	175	175	175	175
General plant overhead	50	65	130	225
Total operating cost, $1,000/yr	480	670	1,420	2,485
Operating cost, ¢/lb carbon	28.8	20.1	14.5	12.5

mg/L TOC). Their calculation showed that 48.2×10^6 BTU's per day would be required for the activated sludge system and 39.4×10^6 BTU's per day for the reactivated carbon system.

In a similar study the United States Army Corps of Engineers found that an independent physical-chemical treatment system would consume less energy and resources than either an advanced wastewater treatment system (AWT) that included biological plus polishing, or land irrigation.[13] The energy consumed for each of these systems is shown in Table 6.

Table 6. Comparative Consumption of Energy for Treatment Systems of Similar Capacity Studied by the U.S. Corps of Engineers

Treatment Type	Energy Consumed — Mega Watts
Independent physical-chemical	350-420
Advanced waste treatment (biological plus polishing)	400-530
Land irrigation (on private land)	1100
Land irrigation (on public land)	1142

A more detailed look at the individual elements of cost associated with the reactivation of carbon is indicated since this process accounts for a major portion of the energy required by the adsorption system.

MONITORING TECHNIQUES

Monitoring of a carbon adsorption system refers to measurement of the organic contaminants in the influent and effluent; it does not mean a measurement of the carbon itself. Monitoring of this system is required for the following reasons: (1) insure that the treatment objective is consistently being met; (2) determine when the carbon needs to be reactivated; and (3) provide a baseline of information which is necessary in investigating problems that may develop in the adsorption system.

The frequency and type of monitoring which is required are site specific and are dependent on the frequency of carbon reactivation and the specific treatment objective. A system in which the carbon needs to be changed every day will obviously require more frequent monitoring than one in which the carbon needs to be changed only every six months. Regardless of the actual number of analyses to be performed, the objective of a good monitoring program remains the same - to provide useful information at a reasonable cost. The program should consider several ways by which that end might be served. If the treatment objectives are COD or BOD_5 removal tests should be conducted to see if a relationship exists between these parameters and TOC. The use of TOC is encouraged since it is a way of obtaining information at low cost. Assuming TOC is used as a surrogate parameter, COD or BOD_5 could be run on a spot check basis or as necessary to confirm the relationship and to meet discharge permit requirements. If the treatment objective requires the total removal of a number of priority pollutants, the tests should be conducted to see which of the compounds will first leak or break through the carbon columns. Monitoring for the least adsorbable priority pollutant will reduce costs, while guaranteeing that the remaining priority pollutants are being controlled.

In a well-designed adsorption system, the carbon will be completely spent before it is replaced with virgin or reactivated carbon. The time to replace it is usually when the concentration of the organics in the effluent is the same as in the influent. This can occur in pulse beds or fixed beds in series systems.

When the carbon is reactivated on-site the conditions for reactivation are controlled so that the reactivated carbon is as effective as virgin carbon. The quality of the reactivated carbon can be determined by conducting comparative adsorption tests and standard carbon quality tests as iodine and carbon tetrachloride numbers and apparent density. The latter can usually be corrected with one or more of the other tests for a given application. It may then be used by plant operators to control the reactivation process.

FUTURE DEVELOPMENT NEEDS

The use of adsorption in treating industrial wastewaters is important today, and it will grow more so in the future. Full use, however, is retarded by a number of problems that have been experienced in the design and application of the process. Each of the following problems, in particular, represents a significant research need.

Simpler Analytical Tools & Tests Required

Existing dynamic experimental tests to establish key design parameters for an adsorption system are very time consuming and expensive. Faster and less expensive techniques than these utilizing carbon column studies are needed.

More Efficient Reactivation Technology Needed

Techniques and procedures must be improved in order to minimize energy utilized in reactivating carbon and to reduce carbon burning and attrition losses during reactivation.

Improved Materials of Construction for Adsorption Systems Needed

Since a carbon-water slurry is quite corrosive as are many industrial wastewaters, the improvement of anti-corrosive vessel linings and the selection of the correct materials of construction for other system components is extremely important. Although some work has been done in this area, more needs to be done.

Improved Materials of Construction for Reactivation Systems Needed

The complete destruction of halogenated organic compounds in a thermal reactivation furnace can cause problems particularly for such equipment as furnace rabble arms and teeth, flights in the rotary kilns, belts and tubes in the infrared furnace and vertical tube-type furnaces. It is obvious the improvement of materials of construction is a key factor in minimizing these problems. It has also been observed that inorganics may attack the refractory lining of reactivation equipment. More work must be done in this area to assure availability and proper selection of the correct type of refractories, and/ or to remove the refractory attacking inorganics from the spent carbon prior to reactivation.

Improvement Needed In Adsorption System Underdrains

An underdrain is the so-called heart of an adsorber. It must provide good distribution, be of proper materials of construction, and be sturdy enough to handle high backwash water rates. More work is needed in this area to assure proper design of underdrains.

More Effective Methods of Recovery Needed

Activated carbon serves as a mechanism for concentrating organic materials in wastewaters. Treatment costs, in a number of applications, could be significantly reduced if a practical technology for recovering valuable organic chemicals from spent carbon was available. Low boiling chemicals have been successfully recovered using steam distillation. However, recovery of high boiling compounds has been retarded by unsuitable materials of construction and high energy requirements.

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SEPARATION OF ORGANIC SUBSTANCES IN INDUSTRIAL WASTEWATERS BY MEMBRANE PROCESSES

Ronald F. Probstein, PhD, Calvin Calmon, PhD,
and
R. Edwin Hicks, PhD

INTRODUCTION

Membrane Processes

A membrane is a selective barrier that permits some entities to pass through it while preventing the passage of others. In particular, membranes have the ability to prevent the passage of dissolved molecules while allowing the solvent, usually water, to pass through under the influence of a driving force.

It is the ability to reject particles of molecular dimensions that principally distinguishes a membrane from an ordinary filter. Another distinguishing feature is the fact that the driving force for a filter is always the pressure difference across the filter, which forces the water through while the suspended particles are retained. In the case of membranes there are a number of driving forces in addition to pressure including gradients in concentration, electrical potential and temperature.

The three principal membrane separation processes are reverse osmosis (RO), ultrafiltration (UF), and electrodialysis (ED). Of the three, ultrafiltration bears the closest resemblance to ordinary filtration, in that the process is pressure-driven and the particle sizes held back by the membrane are determined by the membrane pore

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Following receipt of the Ph.D. degree from Princeton University in 1952, his principal work centered in the field of fluid mechanics. About 15 years ago he became concerned with the application of his studies to desalination and water purification and since then he has earned international recognition for his work in these fields. He has been honored for his contributions by election to the National Academy of Engineering and American Academy of Arts and Sciences and by an award from the American Society of Mechanical Engineers.

In 1974 he formed Water Purification Associates to deal with problems of water purification, reuse and pollution control. His activities at W.P.A. since that time have centered on water needs and treatments for synthetic fuel conversion processes.

For more than ten years now he has headed up the water purification activities of the M.I.T. Fluid Mechanics Laboratory and is presently responsible for M.I.T.'s teaching program in water purification, and synthetic fuel production. Among his studies while at M.I.T. have been his use of fluid mechanics to redesign reverse osmosis, ultrafiltration and electrodialysis equipment, resulting in much improved efficiencies.

Dr. Probstein holds a number of patents in water purification and desalination including methods for continuous ion exchange, freeze desalination, continuous flocculation of waste water, and lamella sedimentation. In addition to his texts, he has authored more than a hundred technical papers which have appeared in various scientific and engineering journals. He is a member of many engineering societies, including A.S.M.E., A.I.Ch.E. and W.P.C.F., is a registered professional engineer, and is listed in Who's Who in America.

sizes. However, the pore sizes of a UF membrane are typically some 1000 times smaller than in an ordinary filter. Although reverse osmosis is also a pressure driven process, the controlling factor in particle-rejection is not size directly but generally relates to the diffusion properties of the molecules or ions in the membrane. In electrodialysis, under the action of a D.C. electric field, only dissolved ions are removed or concentrated from the bulk solution based on the selective character of the membrane with respect to particle charge. Since the particles must be charged, the utility of this method for organics separation is limited and shall not be considered further.

One other membrane process applicable to organics separation is liquid-membrane permeation. This process employs a solvent in which an aqueous solution of caustic soda is emulsified. The emulsion acts as a one-way membrane that is permeable only to the organic by virtue of the organic reacting with the caustic soda and forming a compound which stays in place because it is not soluble in the solvent. This procedure will be discussed separately from reverse osmosis and ultrafiltration because of the limited number of organics which can be separated by this method and also because the process is still under development.

In ultrafiltration the selective membrane accomplishes separations in cases where the solute particles to be removed are at least an order of magnitude larger than the solvent molecule, of which the water molecule is of principal interest in this review. On the other hand, in reverse osmosis the membrane can separate out solute molecules which are of the same order or only slightly larger than the water molecule. Reverse osmosis is, however, a relatively high-pressure process with typical applied pressures of 3 to 7 megapascals (MPa) (400 to 1000 psi), compared with ultrafiltration where typical pressures range from 0.07 to 0.7 MPa (10 to 100 psi). The membranes in both processes are fabricated from synthetic polymers with the RO membranes continuous gels and the UF membranes relatively porous materials.

The capabilities of reverse osmosis and ultrafiltration in terms of particle size rejection are compared in Table 1. RO membranes will reject almost completely most species with molecular masses greater than 150. Readily available commercial UF membranes will have high rejections for molecular masses greater than 10,000 and will usually have almost complete rejections for molecular masses greater than 35,000.

Mechanism and Operation of Reverse Osmosis

Reverse osmosis[1-4] is a pressure-driven membrane process that is used to separate relatively pure water from solutions containing salts, dissolved organic molecules, and colloids. Under the action of a hydrostatic pressure applied across the membrane separating the feed from the relatively pure water, the water passes through the membrane and the dissolved materials remain behind.

The Author: Dr. Calvin Calmon is a physical chemist with 43 years of industrial experience. He has been in the field of water and wastewater treatment since he received his Ph.D. degree from Yale University in 1938. Until his retirement in 1973, he worked almost continuously with different divisions of Sybron Corporation, holding important positions with the research and chemical divisions. On his retirement he was Senior Vice President and Research Consultant to the Chemical Group of the Sybron Corporation. Since then he has been a principal of Water Purification Associates and a private consultant.

Most of his industrial work has been in the application of ion exchangers, adsorbents, polymers and membranes to water treatment and pollution control. He has written about 80 technical publications and holds 19 patents in these areas. He is internationally known for his work in the synthesis, development, production and use of ion exchangers. His most recent activities involve the development of treatment methods for the removal of potentially toxic pollutants from industrial wastewaters.

Dr. Calmon has held many important editorial and advisory posts and has frequently been honored for his many contributions to environmental chemistry, including the Distinguished Service Award from the American Chemical Society in 1972 and a Certificate of Appreciation for Contributions to Environmental Chemistry from the Environmental Protection Agency in 1976.

Table 1. Useful Particle Size Ranges of Reverse Osmosis and Ultrafiltration and Reference Particle Sizes

Membrane Process	Particle Size Separated (nm)*	Max. Particle Size for Which Membrane Used (nm)*	Reference	
			Particle	Size (nm)*
Reverse osmosis	>0.3-0.5	-	Water molecule	0.3
Reverse osmosis	-	60-100	Smallest bacteria	200
Ultrafiltration	>3-5	-	10 x water molecule	3
Ultrafiltration	-	3000-5000	Typical bacteria	2000

*nanometer: 10^{-9} meters

Fig. 1 shows the simplest arrangement of a reverse osmosis system consisting of a pump to pressurize the system, usually to pressures of from 3 to 7 MPa, a membrane element, a pressure container to house the membrane element, and controls to regulate the flow and pressure. Normally, a reverse osmosis system is employed with some pretreatment or postreatment which may range from a simple filter to protect the high-pressure pump from particulate matter, to ion exchange demineralization to upgrade the water.

Most reverse osmosis systems in use today employ semipermeable "asymmetric membranes" made from cellulose acetate or polyamide, or "composite membranes" made with a dense thin polymer coating on a polysulfone support film. The asymmetric cellulose acetate membrane is a high-water-content gel structure consisting of a thin rejecting "skin" on the order of 0.1 to 0.5 micrometers thick integral with a much thicker porous substrate 50 to 100 micrometers thick. It is the skin which offers the main hydraulic resistance to the flow. The porous substructure gives the membrane strength but offers almost no hydraulic resistance. The dense rejecting skin of the composite membranes can be up to 10 times thinner than the skin of the cellulose acetate membranes.

The rejection of the dissolved materials is not complete; the incompleteness depends not only on the size of the rejected species, but also on the chemistry of the membrane and the rejected species. With the use of the correct membrane the percent

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The Author: Dr. Richard Edwin Hicks received an M.S. and a Ph.D. degree, both in chemical engineering, from the University of the Witwatersrand, Johannesburg, South Africa. During this time he was employed by the South African Council for Scientific and Industrial Research. His advanced studies were in the field of heat and mass transport phenomena, in particular the optimization of systems containing turbulence promoters as used in reverse osmosis and electrodialysis units for brackish water desalination. Also included was an in-depth study of packed bed transport related to water purification, gasification and liquefaction. He is a principal of Water Purification Associates with 18 years of practice.

Concurrently with his academic studies he was engaged in design and troubleshooting work at the world's first commercial scale electrodialysis plant at the Free State Geduld gold mine in South Africa.

Since joining W.P.A. in 1977, Dr. Hicks has made detailed studies of water problems in coal conversion and oil shale plants in the U.S.A. and has visited several of this country's synthetic fuel pilot plants. He has designed many water treatment plants and, in particular, has been concerned with recycle and reuse of contaminated effluent water.

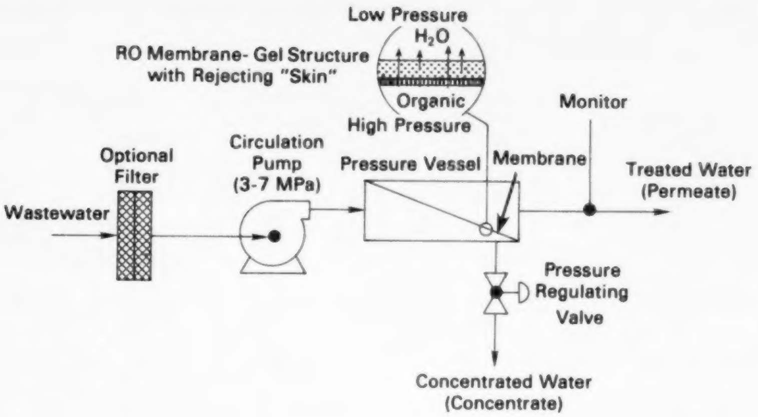
Low Pressure
H_2O
RO Membrane- Gel Structure with Rejecting "Skin"
Organic
High Pressure
Monitor
Optional Filter
Circulation Pump (3-7 MPa)
Pressure Vessel
Membrane
Treated Water (Permeate)
Wastewater
Pressure Regulating Valve
Concentrated Water (Concentrate)

Figure 1. Outline of simple reverse osmosis arrangement.[1]

rejections of inorganic salts will be in the high nineties and there is, as already noted, almost complete rejection of most species with molecular masses greater than 150. The rejection of low-molecular-mass nonelectrolytes, such as small organic molecules, is generally low with the asymmetric cellulose acetate and polyamide membranes. However, with the use of newer composite membranes and by proper pH adjustment, moderate-to-good rejections can be obtained with many intermediate and even low-molecular-mass organics. Because the percent rejections tend to be constant over a wide range of concentration, the concentration in the water passing through the membrane will be proportional to the concentration retained. The higher the fraction of feed which passes the membrane, that is, the higher the "recovery" of water, the higher will be the concentration in the product water. The retained water is often termed the "concentrate" and the product water the "permeate."

If an ideal semipermeable membrane separates an aqueous organic or inorganic solution from pure water, the tendency to equalize concentrations would result in the flow of the pure water through the membrane to the solution. The pressure needed to stop the flow is called the osmotic pressure. If the pressure on the solution is increased beyond the osmotic pressure, then the flow would be reversed and the fresh water would pass from the solution through the membrane, whence the name "reverse osmosis." In actual reverse osmosis systems the applied pressure must be sufficient to overcome the osmotic pressure of the solution and to provide the driving force for adequate flow rates.

Osmotic pressure is a property of the solution and does not in any way depend on the properties of the membrane. For dilute solutions the osmotic pressure is proportional to the mass concentration of the dissolved material divided by its molecular mass, so that at the same mass concentration sugar has a much lower osmotic pressure than salt. For dilute solutions the osmotic pressure is given by the modified van't Hoff equation

$$\pi = i\ c\ (R/M)T \tag{1}$$

where

π = osmotic pressure (Pa)
c = mass concentration (mg/L)
M = molecular mass
R = universal gas constant (8.314 J/mol·K)
T = absolute temperature (K)
i = number of ions formed if the solute dissociates (e.g., i = 2 for NaCl).

In Table 2 are shown typical osmotic pressures of aqueous solutions at the standard temperature of 298 K (77° F).

The amount of water (solvent) that will pass through a membrane is proportional to the excess of the hydrostatic pressure, p, over the osmotic pressure, π, and for commercially useful flow rates p should be large compared to π. The volume of water flux crossing a unit area of membrane per unit time may be written approximately as

$$J = A(\Delta p - \Delta \pi) \tag{2}$$

where Δp is the hydrostatic pressure difference across the membrane and $\Delta \pi$ the osmotic pressure difference corresponding to the solute concentrations immediately adjacent to the membrane surface on both sides. The coefficient A is the membrane water permeability coefficient. It is inversely proportional to the thickness of the solute rejecting portion of the membrane, a quantity which is generally not known precisely. The value of A is determined empirically using Eq. (2).

Although the solvent flux is inversely proportional to the "active" thickness of the membrane, the solute rejection is independent of this thickness. The driving force for the solute flux is mainly the difference in solute concentration across the membrane between the feed and product. Increasing the applied pressure increases the water flux proportionally more than the solute flux, with the result that the quality as well as the quantity of product increases with increasing pressure.

As already observed, the rejection characteristics of the membrane are generally better the smaller the membrane pore size as compared to the solute molecule, while the solvent flux increases with decreasing membrane thickness. Although Reid and Breton[4], during the period from 1957 to 1959, found that cellulose acetate was capable of rejecting electrolytes from aqueous solutions, they concluded that such membranes could not be made thin enough practically to achieve reasonable water fluxes. Loeb and Sourirajan, at about this same period (1958-1961), produced a major breakthrough in membrane fabrication by casting "asymmetric" cellulose acetate membranes which had a very dense, thin rejecting skin on a relatively porous substructure. The thin skin had good rejection characteristics and allowed for practical flux rates because of its relatively low hydraulic resistance, which is proportional to thickness. On the other hand, the integral porous substructure offered little resistance to the flow but provided support for the thin skin.

All the membranes have limits in their tolerance to pH, temperature and chemicals such as chlorine and other strong oxidizing agents. Cellulose acetate membranes have greater susceptibility to biological attack and have limited pH range, while polyamide membranes have a wide pH range but have no tolerance for chlorine or other oxidizing agents. All reverse osmosis membranes are also very susceptible to blockage by deposition of solids, a phenomenon termed "fouling." The concentration must never exceed the solubility of the least soluble material in solution, and suspended solids must be removed from the feed stream.

Table 2. Typical Osmotic Pressure Data at Standard Temperature

Dissolved Species	Concentration (mg/L)	Osmotic Pressure (kPa)*
NaCl (M = 58.5)	50,000	4,550
	10,000	833
	5,000	416
Urea (M = 60)	50,000	2,100
	10,000	420
	5,000	210
Sugar (M = 180)	50,000	375
	10,000	75
	5,000	38

*kilopascals

Commercial membranes are generally limited to applied pressures of less than 7 MPa because of compaction, which leads to long-term decline in water flux. Osmotic pressure is one limitation already mentioned. In order to leave an adequate driving force, the maximum concentration reached, which is the concentration of the effluent concentrate, usually should not exceed 3 MPa osmotic pressure. In this regard, it should be noted that passage of water through the membrane tends to carry the solute to the membrane surface and the concentration at the membrane surface tends to be higher than in the bulk of the liquid. This phenomenon is called "concentration polarization" and is reduced by increasing the flow speed and/or by promoting turbulent flow. The extent to which this can be done depends on the module type. As sold today membranes are fabricated as sheets, as hollow fibers, and as hollow tubes. Depending on the membrane geometry they are packaged in four main module types: spiral wound, hollow fiber, tubular, and plate and frame. Details of the module types along with details of the limitations of commercial membranes will be discussed in the section, "Membranes and Module Developments."

Mechanism and Operation of Ultrafiltration

Ultrafiltration[1,6] is also a pressure driven-membrane separation process. Pressures usually from 70 to 700 kPa are applied and water passes through the membrane. Material which does not pass through the membrane includes particulate matter, colloids, suspensions and large dissolved molecules of molecular mass usually greater than 2,000 and more generally greater than 10,000. Rejection is usually close to complete.

From a theoretical point of view, ultrafiltration is like ordinary filtration except that very small particles are held back by the membrane. The size of the rejected particles depends on the pore size of the membrane; a choice of membranes is available. The most common UF membranes are of the Loeb-Sourirajan asymmetric type and, like RO membranes, these have been cast from a variety of polymers including cellulose acetate and polyamides. Today's practical ultrafiltration flux rates are usually within the range 600 to 3,000 liters per square meter per day ($L/m^2 \cdot d$). This range is about 1/200th of the usual practical filtration rates.

In general the flux through the membrane is linearly proportional to the applied pressure difference across the membrane since in ultrafiltration osmotic pressure effects are usually negligible (see Eq. 2). The accumulation of solutes or particulates at the membrane surface is termed concentration polarization, as in reverse osmosis, and it can give rise to an apparent fouling of the membrane. The effect of dissolved solutes is better understood than the effects of accumulated particulates and undissolved species.

At sufficiently high solute concentrations at the membrane surface, gelation of the macromolecular solute can take place. This gel formation is similar to cake formation in ordinary filtration. When gelation occurs the permeate flux is controlled by the transport rate through the gel layer, which is lower than through the membrane, and it approaches a limiting value independent of the membrane permeability and applied pressure. This effect can be reduced by increasing the velocity of the solution past the membrane in order to "mix up" or "sweep away" the accumulated layer and thereby reduce the solute concentration at the surface. This effect is illustrated in Fig. 2. The module types used in ultrafiltration are similar to those for reverse osmosis.

MEMBRANE AND MODULE DEVELOPMENT

The development of the asymmetric Loeb-Sourirajan membrane was an outgrowth of work sponsored by the then Office of Saline Water of the U.S. Department of the Interior. The goal of the work was the desalination of saline waters, and until recently most of the applications of reverse osmosis have been in this direction. Although not normally considered a wastewater application, reverse osmosis has been extensively used for processing foods, such as concentrating fruit juices and sucrose solutions. However, pollution control has often been a byproduct, as in its application to whey processing. With the more recent development of ultrathin composite membranes, reverse osmosis is becoming an important process with exciting potential for the separation of low molecular mass organics. It is beginning to be applied extensively for water reuse, organics recovery, and pollution control. Ultrafiltration, on the other hand, has long been employed for the separation of high molecular mass organic materials and for pollution control applications in the treatment of organically contaminated wastewaters.

Parallel with the advances in membrane fabrication there have been a number of developments in the assembly of membrane modules. Most of the module development efforts have had as a goal the reduction of the polarization and fouling effects which limited flux, without at the same time incurring energy penalties in the form of excessive pressure drops through the system.

Membrane Development

The principal types of reverse osmosis membranes that have been fabricated are the Loeb-Sourirajan flat sheet and tubular membranes, hollow fiber membranes and dynamic membranes. All the membranes except the composites have also been developed for UF applications. A review of the state of development of synthetic membranes is given in Reference 8.

It is useful to have some picture of how reverse osmosis membranes reject molecules since it provides some insight into the membrane developments. As already noted, in rejecting molecules, reverse osmosis membranes do so not only by mechanical filter action but also by other mechanisms. Two among these are the solution-diffusion mechanism and the charge-exclusion mechanism. In the solution-diffusion mechanism the movement of each species can be described as a solution of that species in the membrane which diffuses through the polymer matrix under the action of pressure and concentration differences across the membrane. It is easy to visualize that a high-water-content gelatinous membrane will only be capable of sorbing a low salt concentration relative to the external concentration, while the difference in water concentration across the membrane will be small. The

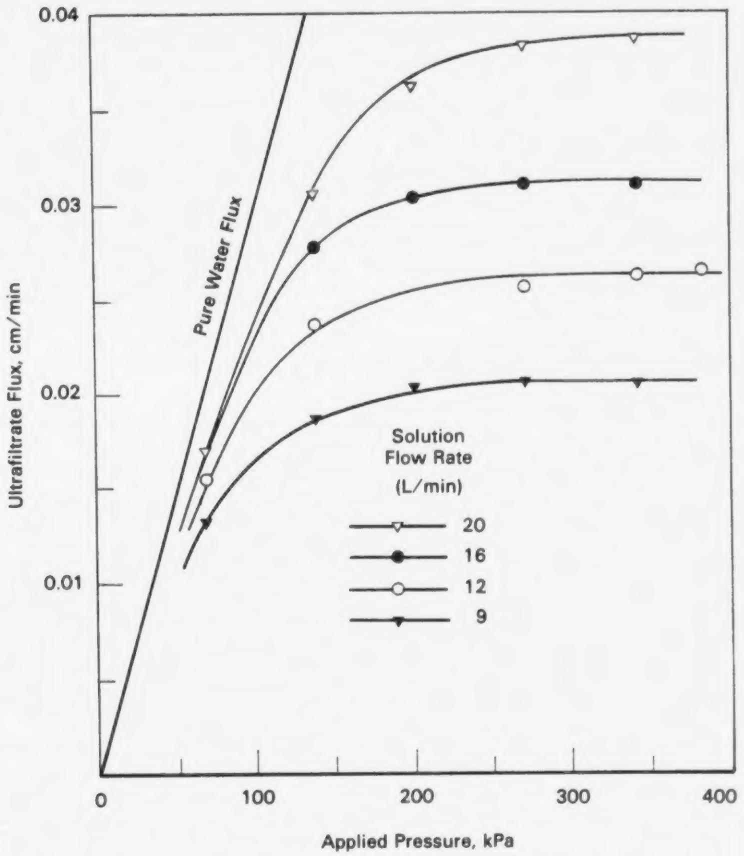

Figure 2. Effect of solution flow rate past membrane on ultrafiltration flux.[6]

charge-exclusion mechanism is applicable to ionized solutions, whereby the membrane in contact with the ionized solute acquires a charge of opposite sign, as do cellulosic materials, and thereby acts to slow down the movement of charged particles through it.

Loeb-Sourirajan Membranes—

These membranes were originally "cast" from a solution of cellulose acetate dissolved in an acetone solvent. The viscous solution is spread on a glass plate and the solvent allowed to evaporate. This forms the thin skin at the solution-air interface with the underlying solution still fluid below. The membrane is then "quenched" by plunging it into a cold-water bath. The water diffuses into the interior of the film, serving to precipitate the remaining polymer with consequent gelation. In this quenching the porous backing is formed. The membrane is then peeled off the glass. The solute rejection properties of these membranes were not good and Loeb and Sourirajan found that by "annealing" the membrane in hot water for a suitable period the strain was removed, the polymer shrank, and its porosity decreased, giving the membranes better rejection properties although lower permeabilities.

Cellulose acetate membranes are today routinely manufactured for commercial use. They have water permeabilities in the range 600 to 1,200 L/m²·d at 5.5 MPa with salt rejections from 95 to 99 percent. They do, however, have poor chemical resistance and are hydrolyzed below pH 4 and above pH 8. The membranes are also hydrolyzed above 38°C. The membranes are resistant to chlorine and can be operated continuously with up to 2 mg/L, and for 15 minutes with up to 5 mg/L chlorine. Asymmetric membranes have been prepared from different polymers including cellulose triacetate, aromatic polyamides that are generically related to nylon, and other polyamides. Although some of these membranes exhibit high salt rejections they generally have lower water permeabilities than the cellulose acetate membranes. The polyamide membranes which are in wide use are, however, much more resistant to biological attack and can be operated over a pH range from 3 to 11. Their temperature limitation is about the same as for the cellulose acetate membranes but unlike these membranes, they are not very resistant to chlorine, their limits being 0.1 mg/L at pH <8 and 0.25 mg/L at pH $\geqslant 8$.

Asymmetric ultrafiltration membranes are prepared in the same way as the reverse osmosis membranes, except that they are much more "open" membranes and have correspondingly higher permeabilities. These membranes also have been cast from a wide range of polymers with the aim of seeking better solvent resistance, pH resistance, and thermal stability. Antifouling ultrafiltration membranes have been prepared from sulfonate polymers[9]. These polymers incorporate the negatively charged sulfonate group, derived from sulfuric acid. This charged group tends to prevent adherence to the membrane of colloidal foulants in the water, most of which are negatively charged. Table 3 shows some properties of asymmetric membranes produced by the Amicon Corp. and used for organics separation.

Hollow Fiber Membranes—

One asymmetric membrane geometry which has been fabricated that enables the more effective use of polymers with lower permeability is the hollow fine fiber. These fibers are about the thickness of a human hair. Because of their small diameter they permit the packaging of large surface areas per unit volume of container. DuPont has pioneered the hollow polyamide fiber membrane. The fibers, which are actually thick-walled pressure vessels, have an outside diameter of about 80 micrometers and an inside diameter of about 40 micrometers. The feed flows outside the fiber countercurrent to the product water, which flows inside as shown in Fig. 3. The DuPont fiber has a product flux of about 75 L/m²·d at 2.75 MPa, which is about an order of magnitude less than for the cellulose acetate membranes. However, the surface area packing densities are on the order of 40,000 m²/m³. Dow Chemical Co. has fabricated a cellulose triacetate hollow fiber membrane with a flux rate of 60 L/m²·d at 4 MPa. These membranes generally have greater resistance to biological attack and higher salt rejections than the more commonly used cellulose "diacetate," although the water permeability is lower.

As may be expected, because the spacings between the hollow fibers are small they are subject to clogging, and extensive pretreatment of even relatively clear waters must be carried out.

Hollow fiber membranes are also produced for ultrafiltration applications, although generally the internal diameters of the fibers are from 10 to 30 times larger than the DuPont fibers.

Composite Membranes—

The composite membranes mentioned earlier are a more recent development of particular importance in organics separation since they allow for greater ease in tailoring the membrane properties. These membranes are prepared by casting a dense, homogeneous ultra-thin polymer film onto a relatively porous substrate. Different

Table 3. Amicon Corp. Ultrafiltration Membranes

Membrane	Mol. Mass Cutoff	Water Flux @ 380 kPa (L/m²·d)
UM 05	500	150-300
UM 2	1,000	450-850
YM 5	5,000	1,150-1,700
YM 10	10,000	1,700-2,600
YM 30	30,000	4,800-29,000

polymers can be used for the two layers, each having the best property for its particular function. These thin-film composite membranes are now fabricated with rejecting skins a factor of ten times thinner than the skin of the cellulose acetate membranes. Not only does the thin skin permit much higher water fluxes, but polymers can be used which have higher rejection capabilities and which are more chemically and thermally stable. The successful flat sheet composite membranes developed originally by North Star Research and Development and now made by FilmTec Corp. are composed of either a sulfonated polyfuran or PEI (polyethylenimine) film on a polysulfone support film[10]. These membranes show very high salt rejections at high flux rates. They do, however, suffer from low resistance to chlorine. Recently, FilmTec has developed a new membrane of proprietary composition (FT-30) which shares some of the properties of the original North Star membranes but which shows appreciable resistance to degradation by chlorine[10,11]. On simulated sea water, salt rejections of 99.5% are reported with flow rates of 1,200 L/m²·d for pressures of 7 MPa at 25°C. Thin film composite membranes with similar properties are also made by other manufacturers[12,13].

Another advantage of the composite membranes which may be mentioned is their improved resistance to long-term compaction. The organics separation capabilities of these promising membranes will be discussed in the next section, "Organics Separation by Reverse Osmosis."

Dynamic Membranes—

Because irreversible fouling so often limits the membrane life, a great deal of work has been done on dynamically formed membranes. The membrane is made by depositing, from a slurry, inorganic-ion-exchange materials such as zirconium oxide or organic polyelectrolytes such as polyacrylic acid. The deposit is formed inside porous tubes. When the dynamically formed membrane is fouled it may be pumped out of the tubes and replaced *in situ* without moving the tubes. In general, the rejections of these membranes are somewhat lower than the rejections of "permanent" membranes. However, extremely high fluxes are reported with values of 4,000 to 8,000 L/m²·d at 6.5 MPa. The reproducibility of these membranes does present some problems. The membranes are also useful for ultrafiltration applications.

Module Development

The membranes described in the previous section are normally packaged for both reverse osmosis and ultrafiltration applications in one of four configurations: spiral wound, hollow fiber, tubular, or plate and frame. The two most commonly used configurations are the spiral wound and hollow fiber.

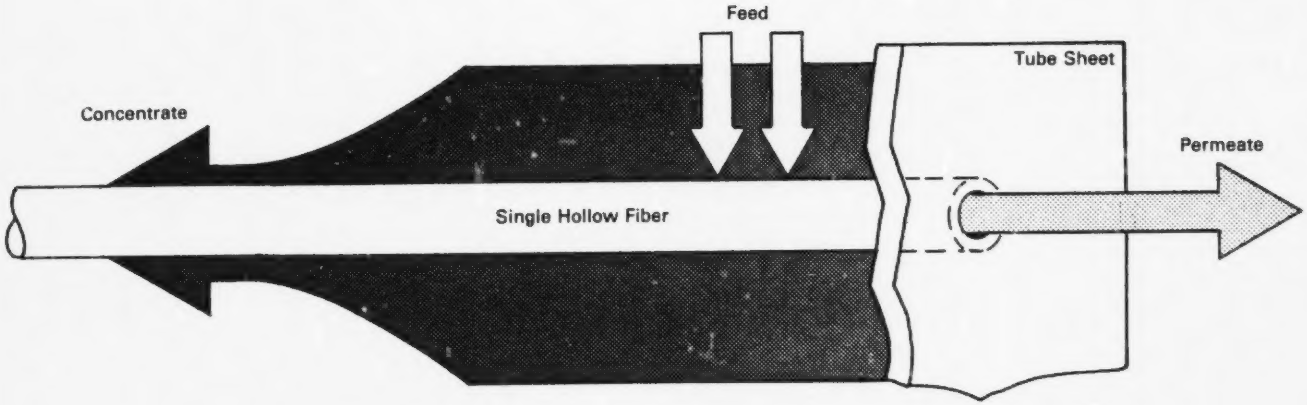
Feed
Tube Sheet
Concentrate
Permeate
Single Hollow Fiber

Figure 3. Hollow fiber flow configuration.

The concept of the packaging of the spiral wound module is shown in Fig. 4. The configuration consists of two sheets of membrane sealed on three edges to form a flexible envelope, or leaf. The open end of the envelope is attached to a perforated central tube. A mesh-like spacer is placed adjacent to the membrane envelope and the layers are wrapped around the central tube like a window shade. The function of the spacer is to separate the membrane layers so that the feedwater can flow axially between the leaves under pressure and also to promote turbulence in the feed stream. Permeate flows through the membrane into the support fabric and is conducted spirally to the perforated central tube where it is collected and removed.

The spiral wound module has the advantages of a high packing density, low manufacturing cost, and relative ease of cleaning by both chemical and hydraulic means. Its main disadvantage is that it cannot handle feeds containing suspended solids without extensive pretreatment because the feedwater flow passages are thin and subject to clogging.

The hollow fiber module is shown in Fig. 5 in the configuration developed by DuPont. The fibers are packed together in a cylindrical bundle about a central feedwater distributor tube. The fibers are bent in a half-loop with the free ends potted in epoxy resin at one end with the bores of the fibers exposed. The bundle is placed in a pressure vessel. The pressurized feed is introduced through the distributor tube and flows outside of the fibers (see Fig. 3) with the permeate passing through the fiber walls into the bores of the fibers. The permeate flows up through the bores to the open fiber ends at the epoxy head. The concentrate is removed from the opposite end of the unit.

As already noted, the packing density of this configuration is very high, with the result that hollow fiber systems are compact. In addition, the capital cost is relatively low. The main problem with this module is that it is very susceptible to clogging because of the small spacing between the fibers. It is also very difficult to clean. For these reasons, hollow fiber units usually require expensive pretreatment for removal of materials which might plug them.

The tubular configuration is illustrated in Fig. 6. The membrane is either cast on the inner surface of a porous tube or placed within the tube, which is typically 1 or 2 cm in diameter. A module is normally formed by connecting a number of tubes in series or in parallel. The feedwater circulates through the tubes under pressure and the permeate drips off into a collection system for removal. These systems present a relatively small membrane area per unit volume of feed and therefore have high capital costs. However, they do have the advantage of being able to handle feeds containing suspended solids, so long as they do not foul the membranes, and they can be cleaned either mechanically or hydraulically with relative ease.

The last module type is the plate and frame configuration in which membranes are attached to both sides of a rigid plate (Fig. 7). The plates are constructed from a number of materials, including solid plastic with grooved channels on the surface, porous fiberglass materials, or reinforced porous paper. The plate and frame units are put in a pressurized vessel through which the wastewater is fed under pressure. The permeate passes through the membranes, which are in contact with the high pressure feed, and is collected from the plates which are at low pressure. The design is complex and is expensive for large scale use but is useful where sanitary or clean conditions must be maintained.

ORGANICS SEPARATION BY REVERSE OSMOSIS

As discussed previously, most commercially available UF membranes have high rejections for large macromolecular organic species, regardless of the type of species. On the other hand, until recently, the removal of smaller organic molecules by membranes was not widely practiced. Reverse osmosis membranes now commercially available reject the smaller organic molecules with the extent of the rejection for a given membrane dependent principally on the size and type of species.

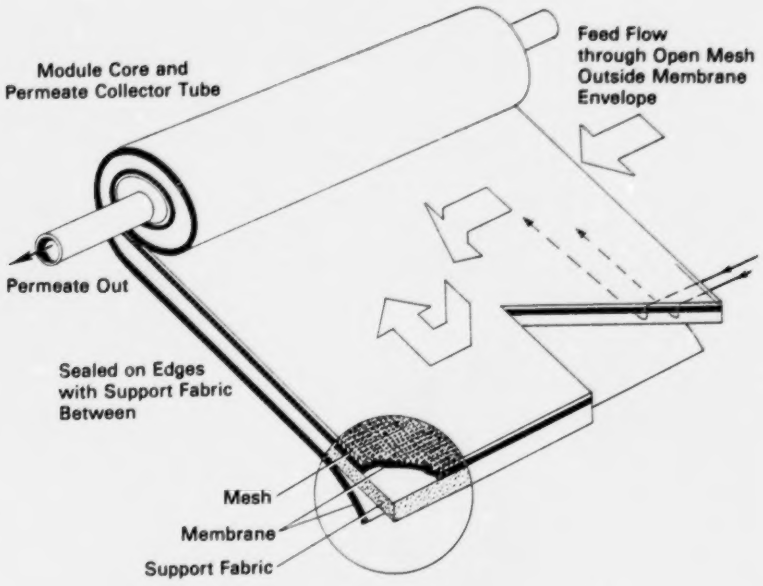

Figure 4. Packaging of spiral wound module.[1]

Large amounts of data on organics rejection by reverse osmosis membrane can be found in the literature. However, there is to date no general methodology for predicting the rejection characteristics of a given compound as a function of such variables as membrane type, solution pH, concentration, temperature, mixture properties, etc. The bulk of data available for organics rejection is from laboratory experiments with single solute aqueous solutions and selected membranes. Generally, the solutes are tested at concentrations maintained low enough that osmotic pressure effects are not important. On the other hand, most field applications of reverse osmosis for organics removal involve complex mixtures of organic compounds at varying concentrations which can make interpretation difficult. Moreover, the availability of such data is limited.

The ability of membranes to handle organic-containing wastes can be conveniently discussed in terms of the several classes of organic compounds. The molecular size of compounds within each class varies greatly and, as discussed, this has an important bearing on rejection. Several other properties specific to each class strongly determine membrane performance[14]. These include the extent to which the molecules are ionizable and the charge on the ion, the solubility of the compound in water and in organic solvents, and to some extent the shape of the molecule. Rejections are further dependent on the type of membrane, whether these be asymmetric cellulose acetate or aromatic polyamide, composite, or dynamic membranes. It may be possible to select an optimum type of membrane for each class of compounds. Operating conditions of temperature and pressure have only a secondary effect on rejection, although these variables largely determine the flux for a given membrane type.

Available data are principally for hydrocarbons and oxygenated compounds, in particular acids and alcohols. From a pollution control point of view other organics, especially nitrogen and sulfur containing species, are important. While some information is available for amines, the nitrogen-containing organic bases related to

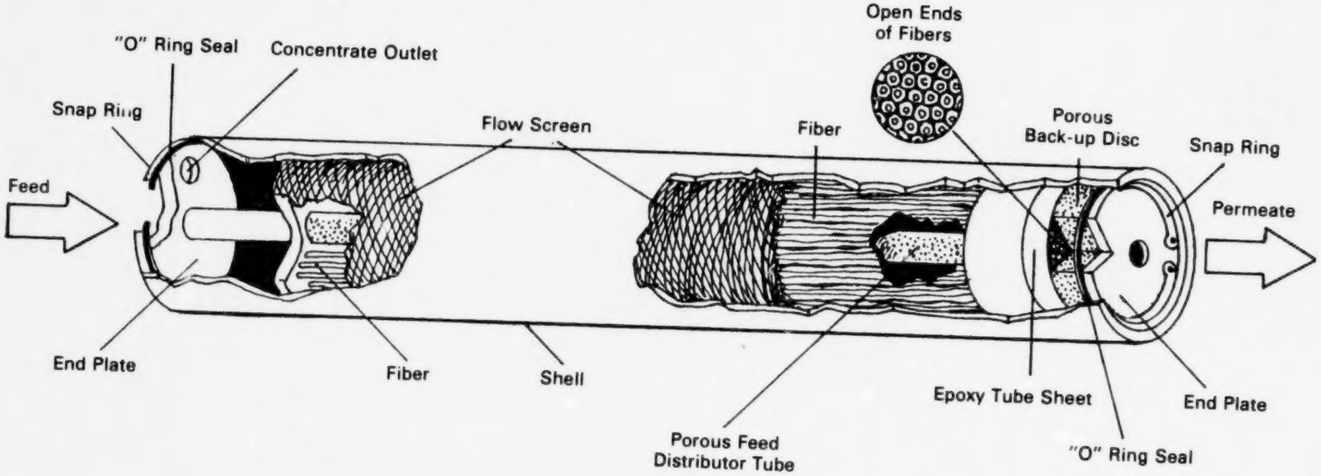
Feed
Snap Ring
"O" Ring Seal
Concentrate Outlet
End Plate
Fiber
Flow Screen
Shell
Fiber
Open Ends
of Fibers
Porous Feed
Distributor Tube
Epoxy Tube Sheet
Porous
Back-up Disc
Snap Ring
Permeate
End Plate
"O" Ring Seal

Figure 5. DuPont hollow fiber module.[1]

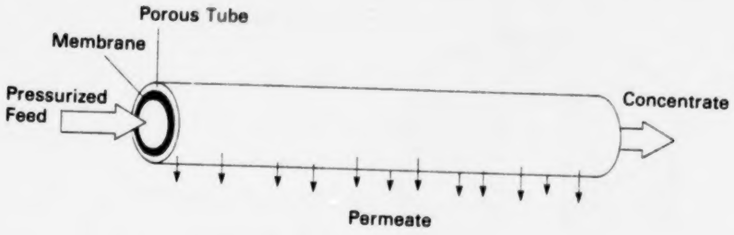

Figure 6. Tubular membrane element.

ammonia, there are unfortunately limited data published for other species important in industrial wastewater control. The Environmental Protection Agency has published a list of 129 "priority pollutants" which are of particular concern in effluent control. Considerable attention has recently been directed towards these compounds although their rejection by membranes has not been extensively reported.

Hydrocarbons

Data for rejection of hydrocarbons by cellulose acetate membranes[15] indicate that the rejection increases with decreasing solubility in water. This is in accord with the solution-diffusion rejection mechanism discussed previously, wherein the solute and solvent dissolve in the membrane material and then diffuse through it. The relative rate of permeation of the solute and solvent through the membrane determines the composition of the permeate. Low membrane solubility of the solute therefore leads to high rejection. Membranes are basically a high-water-content gelatinous substance and the solubility of a species in the membrane is related to its solubility in water. Consequently, all other factors being equal, the rejection of a class of compounds can be expected to increase with decreasing water solubility as was found for the hydrocarbons.

For a given solubility and membrane, the rejection will of course relate to molecular size and also to its shape. For hydrocarbons of equal solubility, rejection decreases in the order

$$\text{aromatics} > \text{cyclic compounds} > \text{chain compounds}$$

Benzene, which forms the basis of the aromatic compounds, has a relatively high solubility and a moderate rejection of about 75%. Chain hydrocarbons of the same solubility have lower rejections in the order of 40%. Compounds with solubilities of less than about 100 mg/L generally have rejections in excess of 90%.

Oxygenated Compounds

These compounds include classes of organics whose degree of ionization in solution can be high, and those which are only slightly ionized in solution. The acids, and the phenols, for example, are ionized at high pH. Other oxygenated compounds including the alcohols, ketones, aldehydes, esters and ethers are only slightly ionizable at any pH. Some of these materials, in particular the aldehydes and ketones, are polar, that is, they have a differential charge across the molecule, and so behave like ions to some limited extent.

The degree of ionization plays a very important part in determining the rejection characteristics of a species, as is clearly shown in Figs. 8 and 9. In general a dramatic

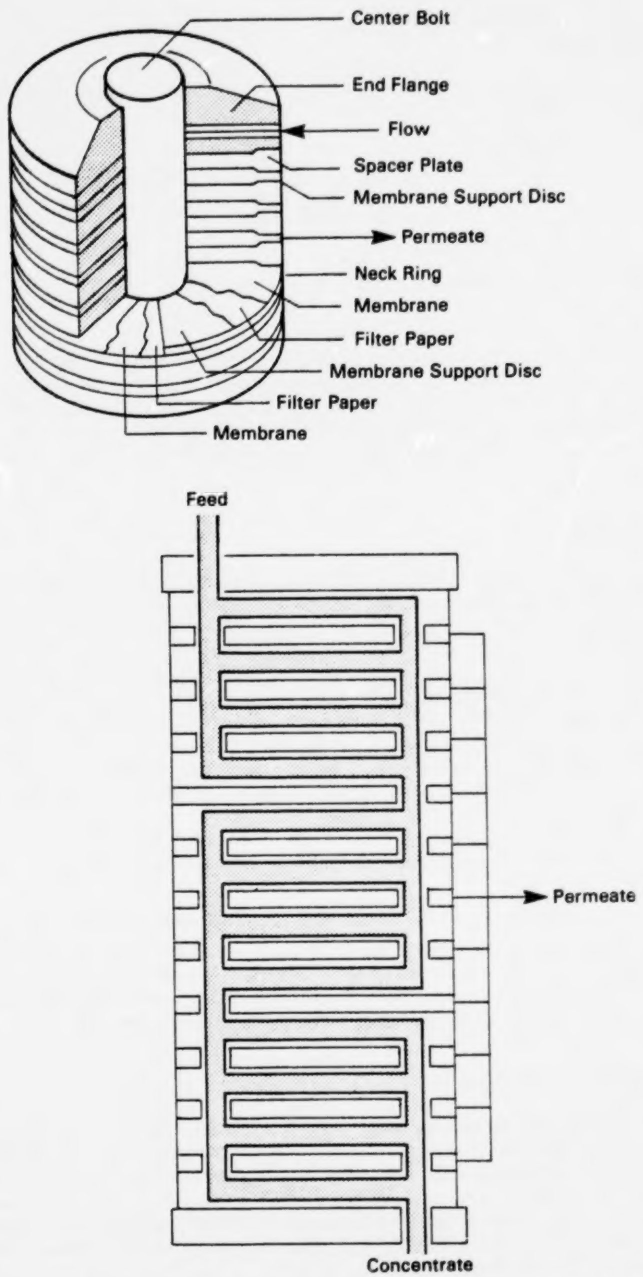
Center Bolt
End Flange
Flow
Spacer Plate
Membrane Support Disc
Permeate
Neck Ring
Membrane
Filter Paper
Membrane Support Disc
Filter Paper
Membrane
Feed
Permeate
Concentrate

Figure 7. Plate and frame membrane configuration showing cross section of membrane unit and flow in module.[1]

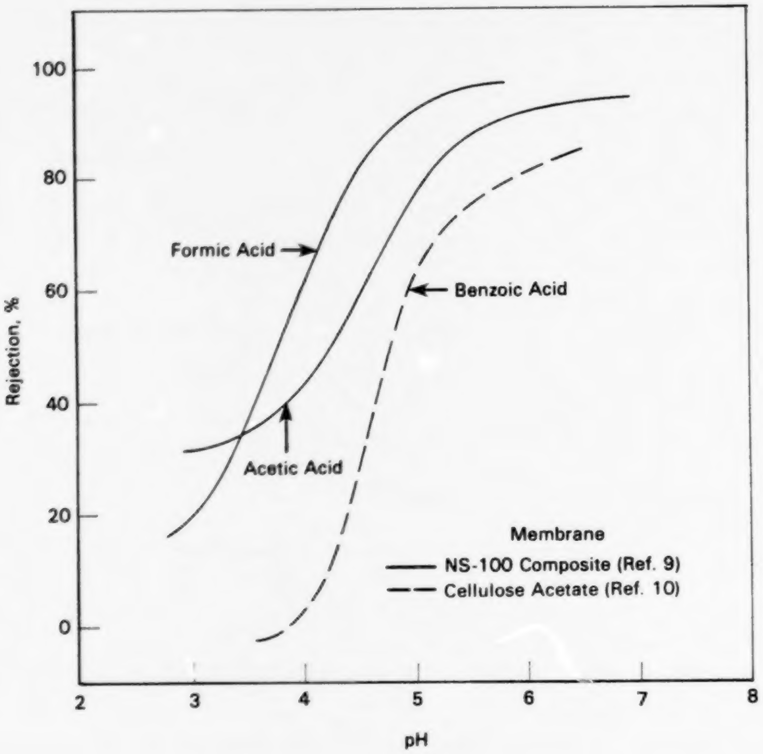

Figure 8. Rejection of carboxylic acids as a function of pH.

increase in rejection occurs in the pH range over which the species changes from mainly dissolved molecules to mainly ions. The predominant rejection mechanism is clearly that of charge exclusion. In this respect it is interesting that while the carboxylic acids are essentially ionized above pH 7, phenols are only ionized at pH's about 9 to 10. As cellulose acetate membranes cannot be used at these high pH's, it was not until the arrival of composite membranes that treatment of phenolic containing wastes by membrane processes became feasible. The composite membranes have a further beneficial effect in addition to their application at low and high pH. Because the active film is considerably thinner than in asymmetric type membranes, they can be significantly more dense or "tighter" for the same flux. Consequently, for the same degree of ionization, composite membranes will generally perform better. This is in principal a size effect.

The availability of these tighter composite membranes has had a tremendous impact on treating nonionizable compounds such as the alcohols, where molecular size appears to predominantly determine rejections. For example, rejections of alcohols by composite membranes range from about 40% for methanol, the smallest alcohol with a molecular mass of 32, to greater than 90% for alcohols greater than propanol, molecular mass 60. Equivalent rejections for cellulose acetate membranes are 1% to 20%[19].

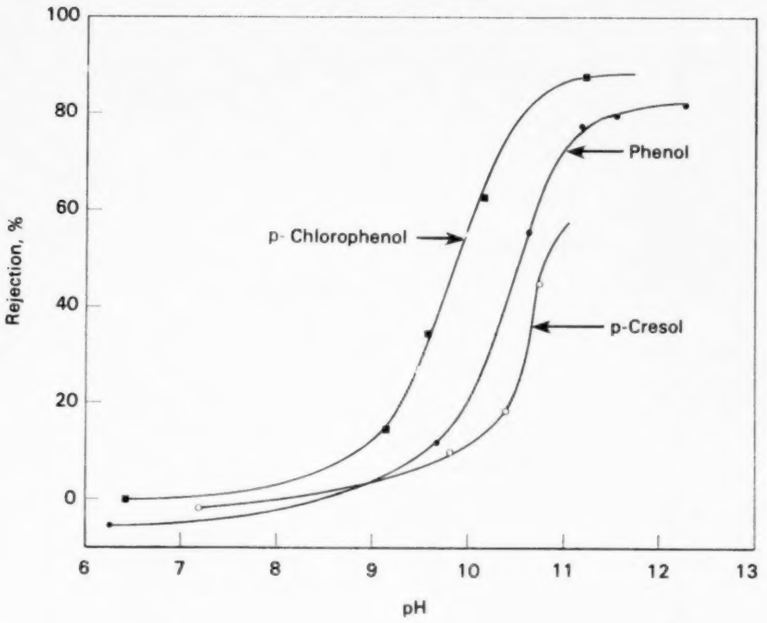

Figure 9. Rejection of phenols by cellulose acetate membranes as a function of pH.[11]

Aldehydes, ketones, esters and ethers also exist as unionized molecules in aqueous solutions. Apart from molecular size, the rejection of these substances can be correlated with their polarity, which for the organic substances discussed decreases in the following order:

acids > alcohols > aldehydes > ketones > esters > ethers

Rejections of ethers are consequently determined essentially by the shape and size of the dissolved molecule[15].

Nitrogen Containing Compounds

The amines are weak bases and dissociate into ions at low pH. As with acids and phenols, the rejection of amines is largely determined by the degree of dissociation as is shown in Fig. 10. Secondary and tertiary amines have higher rejections than primary amines.

Pesticides and Priority Pollutants

Although not belonging to specific classes of organic compounds, pesticides and the priority pollutants are of importance in industrial wastewater control.

Both cellulose acetate and composite membranes showed greater than 98% rejection for chlorinated and organophosphorous pesticides[20]. However it was concluded that a significant fraction of the removal is due to adsorption on the membrane. Long-term data are necessary on the effect of exhaustion of adsorptive capacity on removal of pesticides, and procedures for extraction of adsorbed pesticides must be developed.

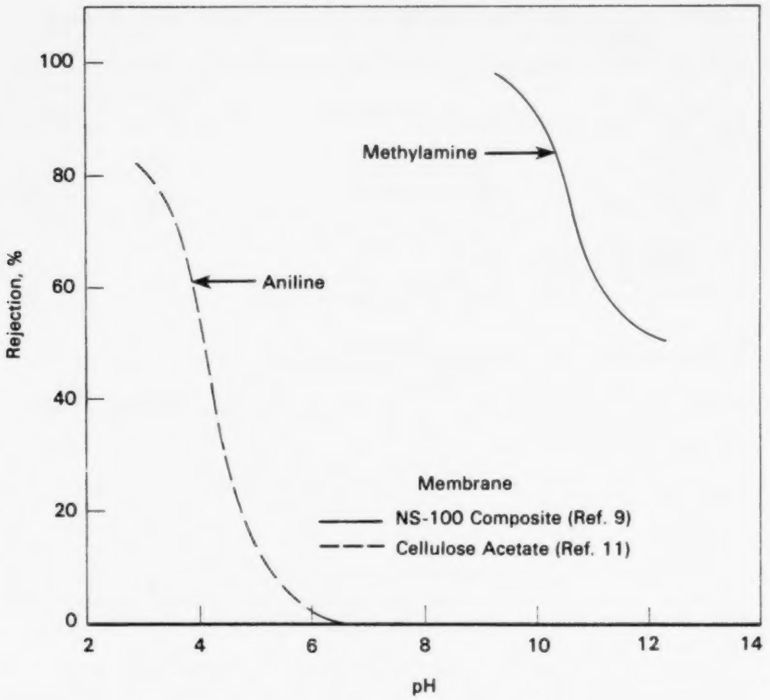

Figure 10. Rejection of two amines as a function of pH.

Data available for removal of organic priority pollutants by reverse osmosis are summarized in Table 4. Removal of trace organic pollutants can be enhanced by proper selection of the membrane and operating conditions, pH adjustment if the compounds are ionizable, and complexation of the compounds with high molecular mass substances, such as humic acids in natural waters.

INDUSTRIAL APPLICATIONS

Textile Industry

Both ultrafiltration and reverse osmosis have been successfully applied, on pilot scale, to the treatment of textile effluents for the reduction of wastewater volume and the recovery of water, process chemicals and heat[24-26].

The ultrafiltration of effluents from the scouring of raw wool results in a clear permeate, which can be recycled or reused, and a concentrate containing the wool grease, which can be subsequently recovered and refined into lanolin. Similarly, ultrafiltration of effluents from the desizing of fabric permits separation, recovery and recycle of water and sizing agent. In both applications, the flux through the ultrafiltration membrane decreases with time due to concentration polarization and possible gel formation and blinding of the membrane. Since ultrafiltration removes

Table 4. Rejections of Some Organic Priority Pollutants by Reverse Osmosis

	Membrane	Rejection (%)	Reference
Hydrocarbons			
Benzene	Cellulose acetate	75	21
Toluene	Cellulose acetate	72	21
Ethylbenzene	Cellulose acetate	78	21
Chlorinated Hydrocarbons			
Trichloroethylene	Aromatic polyamide*	>74	22
Tetrachloroethylene	Poly (ether/amide) composite	>93	23
Esters			
Dimethyl phthalate	Poly (ether/amide) composite	95	23
Phenols	—	pH dependent	See Fig. 9
Pesticides	—	>98	See Text

*DuPont B-9 hollow fiber.

organic compounds by a sieving mechanism, recycle of the permeate to the process will result in a buildup of low molecular mass compounds dissolved in the process water. Discharge of a portion of the permeate is necessary if the buildup is detrimental to the process.

Reverse osmosis has been used for recovery of up to 90% of the water from effluents of textile finishing plants. The quality of the permeate is satisfactory for reuse in scouring, bleaching, dyeing and finishing processes. Specific pretreatments over and above cartridge filtration may be required, depending upon the membranes used. Cellulose acetate membranes, for example, require pH control to minimize hydrolysis; hollow fiber membranes are susceptible to plugging and may require extensive prefiltration; and poly (ether/amide) membranes require the reduction of residual oxidizing agent such as peroxide in effluent from bleaching processes.

Tests with cellulose acetate and dynamically formed zirconium oxide-polyacrylate membranes showed a sharp decline in flux at the beginning of the test followed by equilibration to a constant value, along with an increase in rejection, suggesting the formation of a secondary membrane from constituents in the feed. For both UF and RO, development of membrane cleaning procedures and optimization of pretreatment, equipment design and operating parameters may improve the long-term flux of membranes in textile applications. Development of membranes which can tolerate high temperatures, such as the dynamically formed membranes, would permit recycle of hot permeate and significant energy savings.

Food Industry

Ultrafiltration and reverse osmosis are used in the food industry for concentration of process effluents and for separation and recovery of suspended and dissolved solids. Because membrane processes are nonthermal, do not involve phase changes and, in general, do not require chemical addition other than for pH adjustment, they are suitable for recovery of heat-sensitive organics such as proteins. In most food processing applications, UF and RO not only concentrate or recover valuable food products but also reduce the contamination in the effluents to be discharged.

Major problems in the operation of UF and RO in food processing are membrane fouling and membrane cleaning and sanitation. Concentration polarization and formation of a protein gel on the membrane are the usual reasons for decline in flux. Flushing and circulation of cleaning solutions containing enzymes, detergents and/or complexing agents is the most common procedure for restoring the membrane flux.

In the dairy industry, ultrafiltration is used to recover proteins from cheese whey or skim milk[27,28]. Since the membranes are selected for low rejection of lactose and salts and essentially complete rejection of proteins, the composition of the concentrate is controlled as a function of the extent of water recovery. The concentrate can therefore be used as the raw material for a variety of products. Data from ultrafiltration of cheese whey show that gel formation occurs with associated limiting flux (see Fig. 2) when the protein concentration at the membrane surface reaches approximately 20 percent by mass. Optimum operating conditions for the ultrafiltration of whey and milk are determined not only by the tradeoff between flux and energy requirements, but also by the properties of the recovered product. Flux, for example, increases with temperature; proteins, however, are denatured at 55-60° C so that UF is usually carried out at 45-50° C.

Reverse osmosis can be used for preconcentration of cheese whey prior to thermal evaporation with a resulting savings in overall energy requirements[27]. Reverse osmosis is used to concentrate lactose and salts in the permeate from ultrafiltration of cheese whey or skim milk. The nutritional value of the UF permeate is recovered and the RO permeate is recycled or reused. Since the UF permeate is protein free, the flux decline during concentration by RO is primarily due to an increase in osmotic pressure and not to membrane fouling.

The combination of UF for protein recovery followed by RO for recovery of lower molecular mass organics and salts has been tested for other foods including soy extracts and citrus fruit wash water[29,30]. Ultrafiltration has also been used to recover proteins from potato starch process water and fish processing wastewater, and reverse osmosis to concentrate fruit juices and food processing wastewater[31-33].

Oily Wastes

Membranes have proved particularly satisfactory for removing emulsified oils from water[34]. The usual system design is semibatch as shown in Fig. 11. Clean water leaves through the membrane. Oil is concentrated until it separates into a floating layer where it is taken off for burning or recovery. A settled sludge is often also removed. The advantages of this system are that concentrations in the oil layer are very high and the membrane is not exposed to large amounts of free oil which can foul the membranes.

Various sources of oily waste have been treated; for example, the emulsified oils used as coolants and lubricants in machining operations. These oils become degraded and must be disposed. Ultrafiltration can concentrate machinery oils and similar oily wastes from about 3-5% to about 40-50% so that the concentrate can be incinerated without fuel consumption. Fluxes are generally between 800 and 1200 $L/m^2.d$ with permeate concentrations less than 250 mg/L. The permeate can be further cleaned using RO[35].

Pulp and Paper Industry

Membranes have been tested on many wastewaters in pulp and paper plants. Although commercial development is still required, applications involving the recovery of water for recycling show good promise. The initial work has indicated that the best applications are for dilute wastes including pulp and screen wastewaters and bleach plant effluents. Fouling, particularly by fibrous solids, is a problem.

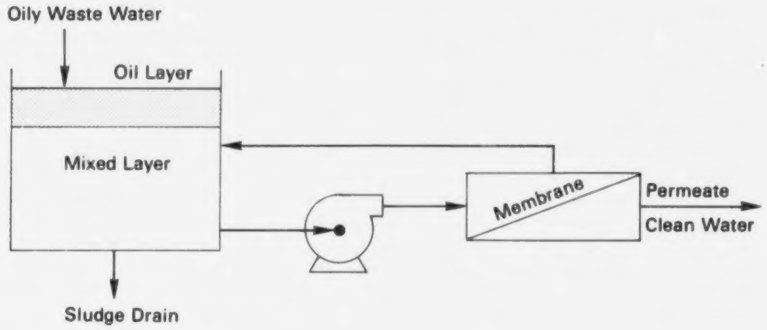

Figure 11. Semi-batch system for treatment of oily wastes.

Dynamically formed membranes seem particularly applicable for color removal. Ultrafiltration has been used for byproduct recovery. The Institute of Paper Chemistry has tested many RO membranes, mostly cellulose acetate, on various pulp and paper mill wastewaters[36]. The wastewaters contained 0.3-2% suspended solids and had a biological oxygen demand (BOD) range of 2,000 to 35,000 mg/L. Flux was limited by fouling and generally ranged between 200 and 400 L/m²·d.

The recovery of commercially valuable chemicals from pulping waste is regularly practiced in the paper industry. Ultrafiltration has been used to recover lignosulfonates which are used as binders in plywood, particle board and other products[37].

Oil Shale Industry

Oil shale retorting produces water, partly by chemical reactions within the retort, and partly by the release of combined and free moisture in the shale. The amount of water produced ranges from about one quarter to one-and-a-half times the volume of oil produced depending on the retorting procedure and site conditions. This represents a significant quantity of wastewater for a 50,000 barrel-a-day oil shale plant and it is essential that a means of reusing or disposing of this wastestream in an environmentally acceptable fashion be available if an oil shale industry is to develop in this country.

Process water that condenses within the retort and is known as retort water has proven to be particularly difficult to treat. This water contains both inorganic and organic contaminants, is black in color and has an obnoxious odor. While the inorganic constituents can be controlled by processes such as steam stripping, chemical precipitation and ion exchange, these treatments do not remove the organics. Nor do the conventional processes for organic control such as solvent extraction, carbon or resin adsorption, and biological treatment have adequate effect. At most a combination of some of these processes results in a 70% removal of the organics which reduces the organic carbon from about 4,000 mg/L to 1,200 mg/L. This is still too high for either disposal or reuse within the plant.

In a search for a feasible retort water treatment scheme, it was recommended that reverse osmosis be evaluated on the basis that it had potential for controlling both inorganics and organics[38]. Several membranes including cellulose acetate and modern composite membranes were tested in the laboratory on actual retort water samples. Screening tests demonstrated that while good inorganics rejection could be obtained under most operating conditions, organics rejections were dependent on pH. At elevated pH's of 10 to 11, using composite membranes, in excess of 95% organics rejection was obtained in a batch cell. The high pH required is a reflection of the acid and phenol content of the retort water.

These exciting results were confirmed in a flow system in which even better rejections were obtained (see Table 5). The flux decline shown with increased recovery in Table 5 is attributable entirely to the increased osmotic pressure. Fluxes were within expectations and suggest commercial application is viable. The economics are particularly attractive in that the expensive inorganic control steps such as ion exchange can be eliminated. Flux deterioration by fouling was not detected in the laboratory, nor in subsequent field tests. However, long term test data are required before the effects of fouling can be fully evaluated.

LIQUID MEMBRANES

Liquid membranes were developed by Li[39] and are formed by dispersing an emulsion of two immiscible phases, for example, an aqueous solution of caustic soda and a hydrocarbon solvent-surfactant solution, in a third phase, for example, an aqueous solution containing phenol. Small emulsion globules, approximately 1 to 5 mm in diameter, are formed upon dispersion and distribute themselves in the third phase (see Fig. 12). Many small "encapsulated" aqueous reagent droplets, having diameters in the range of 1 to 10 μm, are contained in the larger emulsion globules. The liquid membrane is the emulsion between the encapsulated droplets and the third phase and usually contains additives, surfactants and a base material which is a solvent for all of the other ingredients.

The wastewater solution contacts the emulsion in a mixer. The small emulsion globules are stable and do not disintegrate as long as the system is agitated. Agitation maintains good dispersion of the emulsion globules in the wastewater. Organic acids or bases, which are weakly dissociated, permeate across the liquid oil membrane into the very small encapsulated droplets (see Fig. 13). The droplets contain reagents which enhance the permeation rate and neutralize the weak acids or bases. Neutralization converts the acids or bases into salts which are highly dissociated. The insoluble organic solvent or liquid membrane acts as a barrier to the ionic components preventing them from permeating back into the wastewater solution. The ionized salts remain encapsulated inside the emulsion globules. After a certain degree of removal, mixing is stopped and the emulsion globules coalesce and form an emulsion layer which can be easily separated from the continuous wastewater phase. The highly concentrated ionized salt solution can then be separated from the oil emulsion.

Liquid membranes have been used primarily for the extraction of inorganic substances from aqueous solutions and for hydrocarbon separations[41]. A limited amount of data is available on the removal of organics from wastewater[40,42]. Phenols, acetic acid and other organic acids have been removed using a caustic reagent liquid membrane and amines have been removed with a sulfuric acid liquid membrane. For example, wastewater containing 200 mg/L of phenol is treated in a two-stage contactor. The phenol concentration can be reduced to 15 to 25 mg/L in the effluent of the first stage and to 0.25 to 2.5 mg/L in the effluent of the second stage, assuming that only 50 percent of the caustic is spent. The phenol concentration in the caustic can exist in equilibrium with the wastewater even if the phenol concentration in the caustic encapsulated droplet is 10,000 times that in the wastewater.

If a wastewater solution contains other weak acids, they will compete with phenol in permeating through the liquid membrane and reacting with the caustic reagent in the encapsulated droplet. However, if strong mineral acids are present, they will tend not to diffuse across the oil membrane because of their high degree of dissociation and low solubility. Chlorides and sulfates will therefore be excluded from the encapsulated droplet. Thus, the liquid membrane method can be used to remove

Table 5. Reverse Osmosis Treatment of Oil Shale Retort Water

Parameter	Feed (pH 10)	Rejection, %	
		Initial	80% Recovery
Total dissolved solids, mg/L	13,500	99.3	98.7
Total organic carbon, mg/L	4,400	99.5	99.6
Flux (5.5 MPa), L/m^2·d		560	20

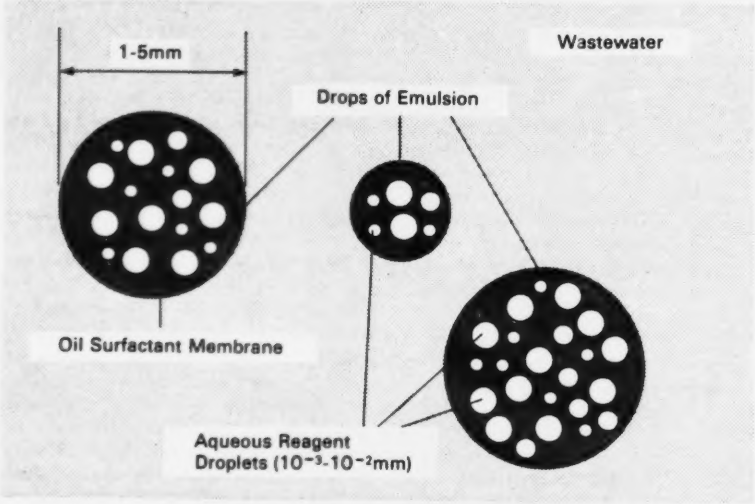

Figure 12. Water treatment by liquid membrane emulsions.[34]

weak acids even in the presence of large amounts of chloride or sulfate. However, in view of the limited data, further development work and testing are required before this system can be considered to be commercially viable.

COSTS

The overall costs of a UF or RO system include the costs of pretreatment and concentrate disposal in addition to the costs for the membrane system itself. Costs for pretreatment depend on both the quality and quantity of the waste stream, and will not be considered here in detail. Values of some 4¢/m^3 (15¢/1000 gal) for filtration to in excess of 25¢/m^3 ($1/1000 gal) for extensive treatment including chemical conditioning and ion exchange may be used as a guide. All costs are in 1980 dollars. In some systems, particularly if emulsified oil is present, UF may be used as a pretreatment to RO, and pretreatment costs will be accordingly higher. Costs for concentrate disposal are specific to the site and type of waste and optimum means for disposal have to be determined for each application.

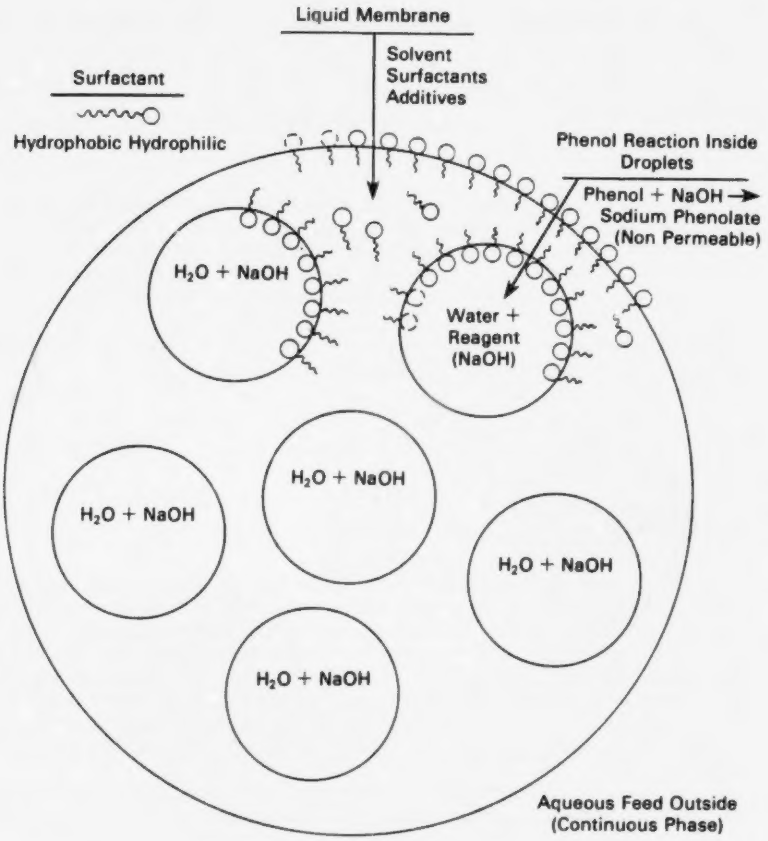
Liquid Membrane
Solvent
Surfactants
Additives
Surfactant
Hydrophobic Hydrophilic
Phenol Reaction Inside Droplets
Phenol + NaOH →
Sodium Phenolate
(Non Permeable)
H₂O + NaOH
Water +
Reagent
(NaOH)
H₂O + NaOH
H₂O + NaOH
H₂O + NaOH
H₂O + NaOH
H₂O + NaOH
Aqueous Feed Outside
(Continuous Phase)

Figure 13. The mechanism of removal of phenol by liquid membranes.[34]

The most reliable means of estimating costs for the membrane system is from current data for similar plants. Experience in the use of membranes for treatment of organically contaminated wastes is limited and we will not attempt to give a detailed cost breakdown. Rather, major equipment and operating costs will be indicated, and engineering factors used to arrive at estimates for overall costs.

Capital Costs

Major capital items include the membranes, the pressure vessels in which the membranes are housed, and the pumps. Reverse osmosis membrane replacement costs range between $40-85/m^2$, with ultrafiltration costs 20 to 50 percent higher. The ultrafiltration pricing appears to be based on higher flux. It is important to emphasize that original membrane cost when computed as part of the manufacturer's total equipment sale price may be only 30 to 40 percent of the replacement cost. More detailed pricing information is not available as such information is treated as proprietary by the manufacturers.

Total equipment and construction costs curves for RO systems[43] can be represented by:

$$\text{Capital \$} = 605\ (Q\ \text{m}^3/\text{d})^{0.86} \qquad [Q < 10^6\ \text{m}^3/\text{d}]$$

These costs include cartridge filtration pretreatment only, and are based on costs for municipal drinking water systems. The equation gives a cost of \$2.9 x 10^6 for a 19,000 m^3/d (5 mgd) plant; reported bids for a similar sized municipal RO system[44] ranged from \$2.5 x 10^6 to \$3.8 x 10^6. The estimated costs for RO treatment of a composite textile finishing plant waste, based on data in Reference 26, is \$2 x 10^6 without membranes, for this flow rate.

Ultrafiltration costs for small systems can be estimated from the following equation based on a tannery unhairing bath wastewater[45]:

$$\text{Capital \$} = 27{,}000\ (Q\ \text{m}^3/\text{d})^{0.7} \qquad [Q < 10^2\ \text{m}^3/\text{d}]$$

Operating Costs

Operating costs are very dependent on membrane life. We recommend that a conservative estimate of, say, annual membrane replacement be made until the extended lifetimes of two and three years, sometimes claimed by manufacturers for municipal systems, are realized in practice with industrial wastewaters. Membrane replacement is generally the major operating expense. The minimum energy required is that needed to pump the feed to the operating pressure. This amounts to about 2 kWh/m^3 for a 5.5 MPa pressure. Total energy required, including that for recirculation for high recoveries, is probably not more than twice this minimum value.

Total operating costs reported in Reference 43 for municipal systems range from \$0.1 to \$0.2 per m^3 for plants of up to 10^6 m^3/d capacity and are in accord with published experience[44]. These costs include maintenance and building energy in addition to the process energy and membrane replacement costs. A membrane replacement life of three years was assumed in these estimates; total operating costs for industrial systems are therefore considered to be some two to three times higher.

Total direct operating costs for UF based on the tannery study[45] are estimated to be about \$1.6/m^3. However, these costs are for a small plant of 11 m^3/d and more than half the operating costs are for labor. Additional economies of scale should be realized for larger UF plants. In this regard we note that economies of scale are not as large as for other chemical processing equipment due to the modular construction of both UF and RO plant. Scaling capital cost with the 0.8 power of the throughput is probably safe.

FUTURE DEVELOPMENTS

Both reverse osmosis and ultrafiltration have been shown to have great potential for the treatment of wastewaters containing dissolved organics. A limitation of currently available reverse osmosis membranes is that they still do not have high rejections for small size, unionized organic molecules. A significant advance in improved rejection characteristics has been made with composite membranes. Further development of these and other membranes that can be more closely "tailored" to reject specific organics is needed[46]. This may be particularly useful with respect to the priority pollutants. Another limitation of current membranes is that operation is generally restricted to below 40 to 50° C. However, many industrial processes and waste streams require treatment at much higher temperatures. Both membranes and membrane systems require development for continuous operation at temperatures of 65° C and higher.

An important practical limitation of both ultrafiltration and reverse osmosis is that the effective treatment of many waste streams is hampered by the fouling of the membrane surfaces by many of the dissolved species. As a result there is a need for the development of membranes which are resistant to fouling, which once fouled can be easily cleaned, and which if fouled are not irreversibly damaged. Moreover, there is also a need for improved module design which through control of the flow can inhibit fouling.

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THE IMPACT OF ORGANIC SUBSTANCES ON WASTEWATER RECYCLING IN INDUSTRY

Robert H. Culver, PhD
and
John F. Donovan

INTRODUCTION

The Concept of Recycling

Recycling is the application of an industry's wastewater to meet all or a part of its water requirements. A distinction is commonly made between recycling and reuse. Recycling in this text is defined as internal reuse: an industry uses a portion of its wastewater again for the same or some other in-plant function. Reuse, on the other hand, involves an industry's use of a wastewater effluent or "reclaimed water" from a municipal or another industrial wastewater treatment facility. Reuse is discussed in another chapter of this monograph.

The concept of recycle in industry is not new. In the United States alone, there are thousands of closed-cycle cooling systems. Noncontact process steam is frequently recycled through a condensate return system for boiler water make-up. Water recycle has been used for a long time in air conditioning and power generation for cooling water. However, while recycle of water in heat-transfer systems has been common for years, attempts to recycle process water have been, in general, relatively recent. Even so, several industries have been engaged in process-water recycling for over 50 years.

The Need for Recycling

Recycling in industry is carried out to reduce operating costs. The cost equation for water use and reuse has changed drastically in recent years. The cost of water is no longer just the cost of pumping it out of the ground or the nearest clean surface water source, plus the cost of cheap energy for heating or cooling it if needed. It now

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includes the cost of expensive energy, the cost of treatment and disposal and the cost of bad public relations if excessive amounts are wasted.

Federal, state and local regulation of industrial discharges has added a significant cost element to the overall cost of water use. Increased water quality requirements by many industrial processes have increased the cost of process water preparation. Increased energy costs have made hot or cold water more valuable. Public awareness of the limitations of the water resource has sensitized management to the value of water conservation and waste reduction.

Recycling therefore is now perceived, in many situations, to be a cost-effective means for supplementing a plant's water requirements. Recycling can often reduce the cost of (a) pumping fresh water (sometimes from great depths), (b) heating or cooling water, (c) treating and disposing of wastewater, and (d) pretreating wastewater before discharge to a publicly owned treatment works or paying penalties for excessive pollution loads. In some cases recycling is essential in meeting the plant's water needs. An added benefit may be recovery of valuable materials previously lost.

Freshwater Use by Industry

The Nation's total withdrawal of water from natural sources in 1975 was about 360 bgd (billions of gallons per day).[1] Industry used about 40 percent of this amount. Table 1 lists the estimated amounts used by the manufacturing industries. The remainder was used by the electric power industry, principally for cooling water.

Status of Wastewater Recycling by Industry

A 1979 study for the Office of Water Research and Technology (OWRT), U.S. Department of the Interior, predicted significant reduction in freshwater withdrawals by the year 2000 for the primary metals, chemical and paper industries due to wastewater recycling.[2] The recycle ratio for these industries, which currently averages about two cycles per unit of water, is expected to increase by that year to about 17 cycles per unit of water.

Industrial wastewater recycling is practiced in most industries in varying degrees. In many, organic substances are absent or are present in concentrations so low that they do not pose processing problems. In other industries, organic substances are used in the manufacturing process and therefore occur in the wastewater, sometimes rendering it unfit for recycle without treatment. The latter industries include petroleum refining, textile manufacturing, coal conversion, polymer and plastics production, pesticide manufacturing and organic chemicals production. However, it is only in recent years that serious widespread efforts have been made by industry to recycle water. While reliable data are not presently available to indicate the degree to which recycling has actually progressed, industries in which recycling is widely practiced are described below.

Petroleum Refining Industry—

The petroleum refining industry involves a complex combination of operations yielding many intermediate and finished products.[3] Typical production processes include crude desalting, crude oil fractionation, thermal or catalytic cracking, solvent refining, grease manufacturing, asphalt production, and product finishing. Among the more common recycling strategies are:

- Recovering wastes from catalytic cracking units and recycling as washwater to the crude oil desalting operation.
- Using stripper bottoms for make-up to crude desalters.
- Using blowdown from high pressure boilers as feed to low pressure boilers.
- Using steam condensate as boiler feedwater and for make-up in cooling towers.

Table 1. Use of Freshwater by Industry, 1975.

Industry	Water Use Billions of Gallons per day	Percent of Total
Primary metals	17.6	34
Chemicals and allied products	13.5	26
Paper and allied products	8.4	17
Petroleum and coal products	2.5	5
Food and kindred products	2.5	5
Transportation equipment	1.3	3
Textile mill products	0.6	1
All other	4.7	9
	51.1	100

These techniques reduce "end-of-pipe" wastewater treatment, which usually involves neutralization or equalization prior to biological treatment. Some plants recycle this treated wastewater as cooling water or scrubber water.

Textile Industry—

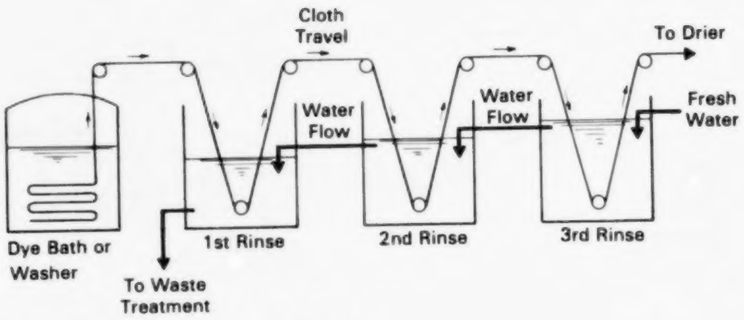
The textile industry is perhaps the most diversified of industries in terms of processes, technologies, and materials employed. One might say that each plant is unique. The materials processed range from cotton, wool, linen and silk, to a seemingly endless list of synthetic manmade fibers. The chemicals employed number in the thousands, ranging from the most complex organic dyes to the simplest inorganic salts, such as magnesium sulfate. The chemicals include dyes, soaps, disinfectants, fungicides, permanent press and waterproofing products, insecticides, acids, alkalies, carriers, fixers and many others.

The value of dyes and other processing chemicals, as well as the cost of water, has for many years provided an incentive for textile engineers to develop systems for recycling and reusing spent solutions. Dialysis for the recovery of caustic soda in the mercerizing process has long been practiced. However, since the treatment of wastewater to control environmental pollution has become mandatory, recycling both water and chemicals is even more economically attractive than before.

One of the largest uses of water, in textile manufacturing, is the washing of the material. Washing is involved in nearly every process, starting with preparation of the raw fibre and ending with washing after dyeing or other finishing of the cloth. Reduction in the amount of water used for washing and rinsing can result in substantial savings. One of the most successful methods by which water can be saved in rinsing is by countercurrent washing. Fig. 1 illustrates the principal of countercurrent rinsing.

Pulp and Paper Industry—

Completely closed-cycle bleached kraft pulp mills have been designed and built.[4] The Great Lakes Paper Company built such a mill in 1976. In this system, the wood room operates entirely on recycled water with the solids being removed by sedimentation, filtration or centrifugation. Screen rejects and other solids are recycled or burned. Unbleached pulp is washed entirely by continuous diffusion using recycled chlorinated filtrate from the bleach plant. Black liquor is evaporated and burned with chemical recovery. White liquor is evaporated in two steps permitting separation and recovery of sodium chloride. The salt is electrolyzed to



Reference: Camp Dresser & McKee Inc.

Figure 1. Countercurrent rinse system commonly used in the textile industry.

produce chlorine and caustic for reuse in the bleach plant. Evaporator condensate from both black liquor and white liquor is used to replace fresh water sources. Recovered sodium sulfate and soda ash are directly reused in the mill.

Organic Chemical Production—

The organic chemical industry is so diversified that even a general description is beyond the scope of this chapter. However, the example of recyling given below illustrates how one plant profited from recycling. In this case a major chemical company manufactured an insecticide for the control of cattle grubs and internal parasites in cattle and sheep. The process generated a high percentage of by-products in the form of tars and a wastewater stream containing dissolved organics and salt.[5] The two tar streams generated up to 650 lbs of waste per 1,000 lbs of product. The wastewater stream amounted to about 18,000 gal per 1,000 lbs of product manufactured.

A pilot plant was constructed to investigate methods of treating the wastewater and recycling valuable compounds. The first step in the recycling process involved blending the tar and waste stream with sodium hydroxide. The second step--the key to the recycling--was high-temperature caustic hydrolysis. This was followed by neutralization and coalescence to achieve separation of the organic phase from the brine. The organic phase consisted of 95 percent pure 4-t-butyle 2-chlorophenol, which was distilled and recycled as a raw material in the pesticide manufacturing process.

The brine was subjected to activated carbon treatment to remove chlorophenol prior to biological wastewater treatment. Regeneration of the activated carbon allowed recovery and recycling of the chlorophenol. By-product recovery and utilization increased yield of the process to approximately 90 percent versus about 40 percent before recycle. Overall waste treatment costs were also minimized by reducing the load on the biological treatment units and by reducing the amount of tar previously incinerated.

Photographic Processing—

One of the few photofinishing companies practicing complete recycle of process wastewater is the PCA International Co., Matthews, North Carolina. In 1977, the company initiated a system, illustrated in Fig. 2, that recycles 90 percent of all washwater and 75 percent of all process chemicals.[6] Process washwater is pumped through reverse osmosis units, which recover 90 percent of the washwater for direct recycling to film and print processing operations. The reverse osmosis concentrate is

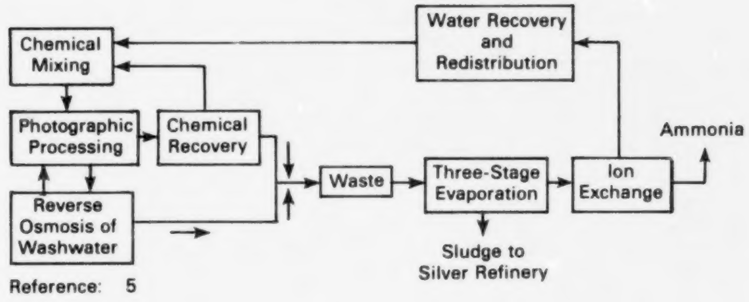


Figure 2. Example of photographic processing recycling system.

combined with chemical recovery wastes and treated in a three-stage evaporation system. The water from the evaporators is condensed, collected and passed through an ion exchange unit. The clean water is then recycled.

Two by-products are the sludge from the evaporation unit and the ammonia from the ion exchange unit. Silver is recovered from the sludge and re-refined. In 1979, the company estimated the value of this silver at approximately $700,000. The ammonia extracted is used to fertilize lawns on the company's 57-acre site.

These brief summaries indicate the diversity of industries which presently employ recycling of wastewater. Others will be described in more detail.

GENERAL CONSIDERATIONS

Approach to Plan Development

Recycling is a highly special activity unique to each plant and therefore, the approach to recycling can be described only in general terms. Recycling can be as simple as returning to the process effluent process water from a particular unit operation, or it can be as complex as providing multistage treatment for all of the wastewater from a large industry with recycle of the treated water for all plant uses (Pulp and Paper Industry). However, regardless of the simplicity or complexity of a recycling scheme, certain information is required before any scheme can be implemented. Each plant must be studied to determine the quality and quantity of the water required for each plant process. Water quality requirements should be developed to define the *minimum* acceptable water quality for each unit process. The effects of each use on quality should be understood. A water use matrix may then be drawn up showing water quantity and water quality needs, and the quantity and quality characteristics of the wastewater discharges available. A hierarchical ordering of uses can be assembled and appropriate treatment processes devised to meet the minimum requirements.

Defining the minimum acceptable water quality for a process is not always easy, particularly where it is proposed to substitute recycled water for water of the highest available quality. Plant managers are understandably reluctant to make changes that may adversely affect the quality of their products. This concern is often justified because of the tendency for pollutants to build up in the recycled stream. Once minimum acceptable water quality standards have been established for each water-using unit process, several strategies are available for designing an appropriate system to maximize recycling and minimize the use of fresh make-up water.

The water quality required by each process might be defined in relatively simple qualitative terms, as shown in Table 2. The wide differences in water quality for

Table 2. Water Quality Limitations on Water Use

Class	Quality	Acceptable Uses
I	Highest quality	Final product wash or rinse, pump seal flush, etc.
II	Some dissolved solids, minor amounts of suspended solids, low color	Make-up washing solutions, first rinse, cooling water, etc.
III	Some dissolved solids, suspended solids and color	Area wash, equipment wash-up

different industries and for different uses within an industry make it impractical to recommend specific numerical limitations for designated water uses except on a case-by-case basis in each plant. This is generally true even within various categories of a single industry. Each plant will have to establish the water quality characteristics required for the individual water using processes within the plant.

Once the minimum water quality requirements for each process within the plant have been established and classified, it then becomes necessary to determine the characteristics of the process waste streams. A comparison of these characteristics with the minimum water quality requirements may show that the wastewater from one process can well serve as the source water for another process within the plant with little or no treatment. For example, a tannery might use the effluent of the last hide-rinsing bath to make up the dehairing solution for the next batch of hides, or a textile factory might use the last rinse of the cloth in a washing operation to make up the next batch of soapy washwater. An example from the food processing industry is the use of the final washwater for vegetables going to canning or freezing as the first wash for fresh vegetables arriving from the field. Such successive use without intermediate treatment is termed *cascading use* of water, in which the wastewater from the unit process is used in another process that can tolerate water of a lower quality.

It is probable that cascading use of water has limited application in most industrial situations, although it should always be investigated to reduce the volume to be treated. In almost every recycling situation some form of treatment will be required before the water can be recycled. The treatment may be as simple as cooling the water in a cooling tower before recycle or as complex as a multi-stage biological-chemical treatment system. Even a system as simple as cooling the water in a cooling tower probably will require chemical treatment to prevent biological fouling and control corrosion.

The conventional unit processes available for treatment of water containing objectionable suspended and colloidal solids for recycle consist of screening, chemical coagulation, sedimentation, filtration and ultra-filtration. Dissolved matter can be removed by such processes as chemical precipitation, ion exchange, reverse osmosis, carbon adsorption, or synthetic resin adsorption, or distillation. For many wastewaters biological oxidation may be used to remove organic material. In some instances chemical oxidation may be advantageous. Typical treatment systems usually consist of a combination of several of these processes.

Recycle of the wastewater from a particular process is often objectionable because of a single characteristic, i.e. suspended solids. In such cases, it may prove feasible and economical to treat the water to remove the objectionable property--for example, to filter out the objectionable solids--and recycle the water directly to the original process. A good example occurs in poultry processing, where cold water used for chilling processed birds may be upgraded by filtration and recycled directly, thereby saving the cost of cooling fresh water. In the textile industry, dilute dye baths or starch solutions have been concentrated by ultra-filtration, with recovery of both the dye or starch and the water. Direct recycle of a process waste stream separated from the general plant wastewater provides the opportunity for conserving energy, product and water. Until recently, the savings inherent in such techniques generally have been overlooked. So far, most treatment for recycling has been concerned with the inorganic materials in the water. Organics have been of little concern in industrial water recycling except in special cases.

Impact of Organic Substances on Recycle

Until recently industrial wastewaters contaminated with organic matter have been considered unfit for recycle and following treatment, have been discarded to the environment, usually to surface waters, there to undergo further degradation as a result of microbial metabolic activity. Biological degradation of organic matter is by aerobic oxidation as long as dissolved oxygen is available in the receiving waters, and thereafter continues as an anaerobic process. The impairments to aquatic life associated with low concentrations of dissolved oxygen are well known as are the gross nuisance conditions that may result from the absence of dissolved oxygen. These need not be detailed here. Now of course industries must remove harmful materials, organic and inorganic, from their wastewaters to comply with the requirements of regulatory agencies. To treat or not to treat is no longer a choice. Since the cost of wastewater treatment is a fixed factor of operation the decision to reuse the treated water is easier to make.

Based on their particular impacts, organic materials in wastewaters may be classified as follows:

- Suspended solids which may contaminate the product, foul equipment or clog pipes or nozzles. Examples are non-soluble fats, feathers, vegetable parts, non-soluble tars, fruit pits, coffee grounds, fish, animal or fowl parts, sawdust and gelatinous chemicals. This list is of course not complete.
- Suspended liquid substances which may contaminate the product, react with process chemicals to reduce effectiveness, or otherwise interfere with processes. Examples are oils, emulsified or free, insoluble organics such as carbon tetrachloride, benzene, dyes or emulsions.
- Dissolved organic substances which may contaminate the product, and react with process chemicals to produce damaging side reactions.
- Examples are: sugars, alcohols, some amines, pesticides, color bodies and similar materials.

Suspended material, both solid and liquid, can be removed by sedimentation/flotation and filtration. Chemical additions may be required to break emulsions or coagulate colloidal or finely divided particles to accelerate their removal by sedimentation/flotation and filtration. Common coagulant chemicals are alum (aluminum sulfate), ferric chloride, lime (calcium oxide or hydroxide) and synthetic polymers. pH adjustment is frequently necessary to assist coagulation. Lime, caustic soda or sulfuric acid are commonly used pH adjusting chemicals. Soda ash and sodium bicarbonate may be used in special situations where the carbonate ion provides a pH buffering action. Chemical coagulation is often effective for color removal. Flotation of materials may often be enhanced by the introduction of the dissolved air under pressure. As the pressure is released fine bubbles attach themselves to suspended substances causing them to float to the surface to form a scum which may be removed by skimming. Solids which settle to the bottom are removed as a semi-liquid sludge. Suspended solids not removed by sedimentation/flotation may be removed by filtration. Some suspended liquids such as heavy oils may also be removed in filters.

A number of processes are available for removing dissolved organic substances including: adsorption on activated carbon or polymeric adsorbents, distillation, reverse osmosis, ion exchange, electro-dialysis and chemical precipitation. The use of activated carbon may involve either passing the wastewater through a bed of granular activated carbon or adding powdered activated carbon to the wastewater in a mixing tank and removing it with the adsorbed materials by coagulation, sedimentation and filtering. Detailed descriptions of the adsorption process are presented in other chapters. In any event pilot studies will normally be needed in each situation where carbon adsorption is being considered.

The types and concentrations of organic substances in industrial wastewaters are as varied as the industries themselves. Their effects on the recycling of the water are usually very specific to the particular system under consideration. For example, small concentrations of colorless organic substances may not affect adversely the recycling of water for dyeing in a textile mill, but even the smallest concentration of colored organic material in a process water will preclude its use for dyeing, especially where pastel shades are used. A similar restriction applies to the manufacture of white paper; however, a slight color is of little importance in the manufacture of brown draft liner board.

The presence of organic compounds in water is often troublesome in the food processing industry where, for example, they can affect product taste in beverage production, and provide a food source for growth of bacteria in poultry processing. Harmful or noxious organic by-products may result from the excessive use of oxidizing agents used as disinfectants.

Problems in recycling wastewater containing organic pollutants are similarly diverse in industries in addition to the food industries. However, such problems are not widespread. In most instances, the organic content as such is of little importance. For example, there are no limitations on the soluble organic concentrations in water used for washing vegetables before canning, although the presence of pesticides or other toxic compounds may be of concern, or for washing and cooling the finished cans. Water used in many industries, including those involved in the manufacture of organic chemicals, production of primary metals, etc., generally requires no treatment at present for reduction of dissolved organic matter. This situation may change, of course, if wastewaters from other types of industries are considered for recycling.

Specific Plant Experience

The following case studies illustrate the use of the processes described above to treat wastewater for recycle.

Chemical R&D Facility—

FMC Corporation's Chemical Research and Development Center at Princeton, NJ meets a "zero discharge" of contaminated wastewater and treats the wastewater to produce a high quality water suitable for recycle.[7] As in any research type laboratory and pilot plant facility, the quality of the wastewater fluctuates widely.

Fig. 3 is a flow diagram of the treatment plant which treats about 14,000 liters per day. The pilot plant wastewater is treated by a rotating biological contactor (RBC), clarification, filtration, and carbon adsorption. The effluent from the latter stage then joins the laboratory wastewater for further treatment. The combined wastes are clarified by coagulation with a synthetic cationic polyelectrolyte, and alum, followed by sedimentation. Final preparation for treatment by reverse osmosis is carried out by a precoat vacuum filter using diatomaceous earth. The pH is then adjusted to between 4.5 and 5.5 to prevent calcium carbonate fouling of the reverse osmosis membranes. Reverse osmosis units recover 81 to 88 percent of the feed water.

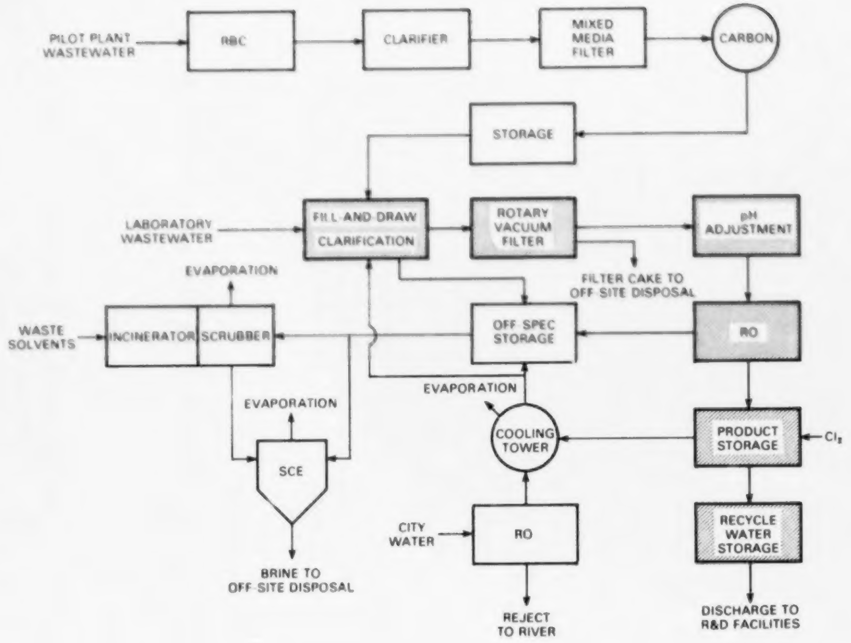

PILOT PLANT WASTEWATER
RBC
CLARIFIER
MIXED MEDIA FILTER
CARBON
STORAGE
LABORATORY WASTEWATER
FILL-AND-DRAW CLARIFICATION
ROTARY VACUUM FILTER
pH ADJUSTMENT
FILTER CAKE TO OFF SITE DISPOSAL
EVAPORATION
WASTE SOLVENTS
INCINERATOR
SCRUBBER
OFF SPEC STORAGE
RO
EVAPORATION
EVAPORATION
COOLING TOWER
PRODUCT STORAGE
Cl₂
SCE
CITY WATER
RO
RECYCLE WATER STORAGE
BRINE TO OFF-SITE DISPOSAL
REJECT TO RIVER
DISCHARGE TO R&D FACILITIES

Figure 3. Flow diagram of advanced waste treatment plant at FMC Corporation's chemical research and development facility.

The quality of the influent water varies widely. The organic content, measured as TOC (Total Organic Carbon), varies from about 200 mg/L to 1,500 mg/L. Selected effluent characteristics are shown in Table 3.

The construction costs (1978) for the plant are shown in Table 4. The total cost for treating and recycling the water was 0.247 dollars per gallon including depreciation (straight line for 10 years), labor, power and materials. The single most expensive material cost was reverse osmosis membranes at 0.0136 dollars per gallon. The cost for a larger scale plant of the same type is estimated at 0.085 dollars per gallon.

Poultry Processing—

The USDA regulations require that the chilling tanks which are part of poultry processing have an overflow rate of at least one-half gallon of water per bird chilled, with the makeup being provided by water of potable quality. At Foster Farms, Livingston, CA, 125,000 gallons of water per day are used in the chiller system. The chiller water is maintained at 34° F.

A recycling system consisting of a pump, a diatomaceous earth filter, two automatic control valves and a heat exchanger for cooling the water to the proper temperature was investigated. A rough schematic diagram of the system is shown in Fig. 4. The results of the treatment as measured by total bacterial count and suspended solids are shown in Table 5. The table shows that the water quality of the chill tank was superior with recycled influent. The bacterial count was only slighter lower but the suspended solids were only 23 percent of those in the conventional chiller.

Furthermore, an analysis of the overall costs indicated that a savings of between $67.84 to $128.34 per day over the existing system in which chiller overflow was permitted to discharge to waste.

Recycling in a Dairy—

Data were collected in Cornell's Animal Science Teaching and Research Center[9] where approximately 350 cows are milked twice each day in a double-ten or rotary milking parlor with appropriate CIP (clean-in-place) machinery. Twelve combinations of three water temperatures with hard and soft water cleaning wash cycles were used to study water and detergent conservation techniques. Special equipment was designed and used to save detergents and washwater for reuse in additional cleaning cycles.

The milking center's double-ten herringbone parlor with a separate identical CIP system for each half made it possible to use one side as a control and the other for experimentation.

Washing and sanitizing a CIP system following milking consists of the following steps in sequence: rinsing, washing with detergent solution, rinsing, sanitizing with a disinfectant solution, and final rinsing. This sequence is called the post-milk cycle. Prior to milking this washing cycle is repeated as a pre-milk cycle. The recycling scheme described below permits the reuse of the detergent solution several times. An additional modification is designed to save water by using the sanitizing solution from the pre-milk cycle (which is essentially uncontaminated since it followed washing and rinsing) to be used for the first rinse in the post-milk cycle.

The basic concept of detergent recycle is illustrated in Fig. 5. During the wash portion of the post-milk cycle, the stored detergent is released into the CIP sink (valve B open). This detergent is circulated through the CIP lines several times by returning and passing it through the detergent storage (valve A open to detergent storage). Thus the detergent does not leave the system during this portion of the cycle. Toward the end of the wash portion of the cycle, the valve at the bottom of the storage tank (valve B) is closed and the detergent is captured. During other portions of the pre- and post-milk cycles, the valve at the top of the storage (valve A) diverts all returning water to waste.

Table 3. Selected Effluent Characteristics at FMC Corporation's Chemical Research and Development Facility[7]

Characteristic	Concentration
TOC	2.0 mg/L
Specific conductance	250 μmhos/cm
Total dissolved solids	248 mg/L
Turbidity	36 NTU
Foaming agents	0.06 mg/L
Color	5 units

Table 4. Construction Cost for Zero Discharge Treatment Plant at FMC Corporation's Chemical Research and Development Facility[7]

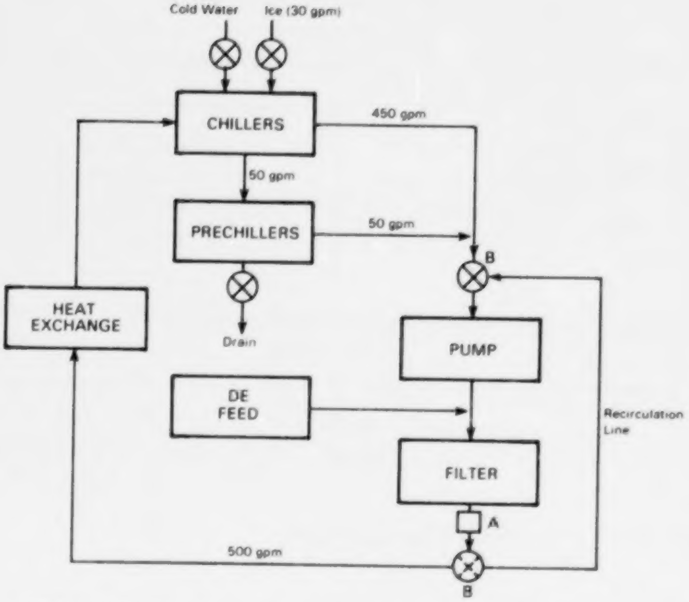
Item	Cost, dollars (1978)
Steel frame building (4,500 ft^2)	550,000
Recycle treatment equipment	223,000
4 Storage tanks for processed water	212,000
Incinerator, evaporator, fuel oil storage tank, collection and feed tanks	624,000
Miscellaneous, cooling tower treatment equipment, chemical feed system, etc.	211,000
	$1,820,000

One modification of the equipment, from the flow shown in Fig. 5, would allow reuse of the sanitizing solution from the pre-milk cycle for the first rinse of the post-milk cycle. The basic concept for detergent recycle with sanitizer reuse is illustrated in Fig. 6. In this modification, during the pre-milk cycle detergent wash step, valves A and B would be open as described above. After the detergent wash was completed and the detergent captured in the detergent storage, valve C would be opened to waste and the rinse water sent to the sewer. Then during the sanitizing step valve C would be turned to divert the sanitizing solution to the CIP sink and from there to be recycled to the CIP lines. The sanitizing solution would then be collected in the CIP sink and valve C adjusted to discharge the subsequent rinse to waste. On the next post-milking cycle the sanitizing solution in the CIP sink would be pumped to the CIP lines to provide the first rinse.

The results of these procedures were presented in a series of bacteriological samples from the two parallel milking lines, one operated in the normal manner, the other with recycled sanitizing solution as described. The results of these tests are shown in Table 6. No significant difference between the two modes of operation is apparent.

It was concluded that -

1. Recycling will save about 60% of the energy and at least 80% of the detergent.
2. Water usage in cleaning and sanitizing may be reduced by about 50%.
3. Savings of about $830/year (1976 dollars) can be made by recycling in a 100-animal dairy.


Cold Water
Ice (30 gpm)
CHILLERS
450 gpm
50 gpm
PRECHILLERS
50 gpm
B
HEAT EXCHANGE
Drain
PUMP
DE FEED
Recirculation Line
FILTER
A
500 gpm
B

NOTE A turbidity meter to detect pressure of DE and control valves. B for safety purposes, that is, prevent DE from entering chiller

Figure 4. Rough schematic program of proposed diatomaceous earth filter system to treat recycled poultry chilling wastewater.

Table 5. Suspended Solids and Total Bacterial Count Comparison of Conventional System and System Using Recycled Wastewater to Chill Poultry

System	Total Bacterial Count (no./mL)	Total Suspended Solids (mg/L)
Conventional chill tank	1.5×10^6	809
DE filter effluent	7.9×10^3	20
Chill tank with recycled influent	1.1×10^6	186

ELEMENTS OF A STRATEGY TO INCREASE RECYCLING

The first need to increase recycling in industry is to make managers more aware of the advantages of wastewater recycling. This awareness can be increased by publication of the results of successful recycling projects and sponsoring of demonstration projects by official agencies.

It is unlikely that any startling new technology will be developed in the near future applicable to industrial recycling. This will continue to depend upon the selection of

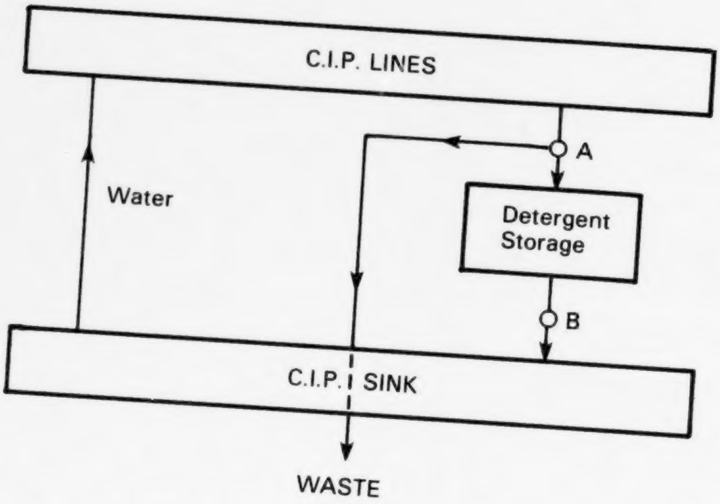

C.I.P. LINES
A
Water
Detergent Storage
B
C.I.P. SINK
WASTE

Figure 5. Initial milking parlor recycle system.

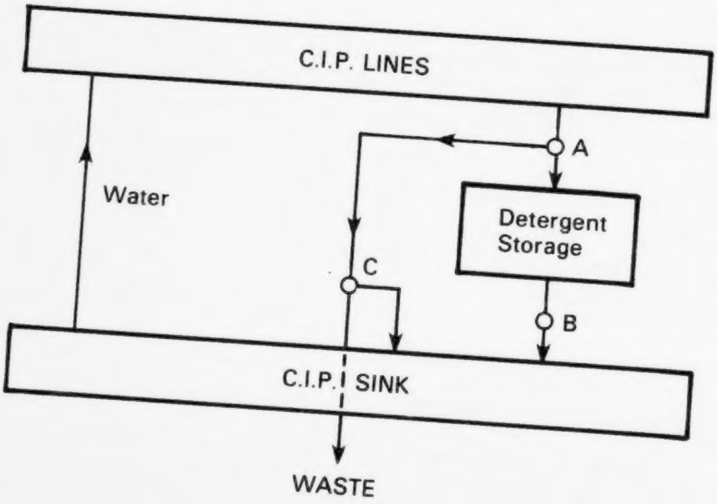

C.I.P. LINES
A
Water
Detergent Storage
C
B
C.I.P. SINK
WASTE

Figure 6. Modified milking parlor recycle system.

an appropriate combination of unit wastewater treatment processes to achieve the desired water quality. Existing unit processes will require modifications to meet individual needs. For example, materials of construction may have to vary from those traditionally used to prevent corrosion in some cases or to protect recycled water quality in other cases. Another example would be the development for a particular application of a microporous membrane having the exact porosity needed to minimize the passage of undesirable organic materials while at the same time maximizing the water flux. The use of polymers which would reduce evaporator tube fouling when distilling water containing organics is needed.

Instrumentation is needed to monitor automatically trace quantities of specific organics in the recycle stream to prevent product contamination. If operators could be assured that the recycled water met quality standards at all times they would be more receptive to its use. Detection methods are available such as TOC (Total Organic Carbon) analyzers but they have to be modified and developed for on-line use.

Two of the case studies in this article, the dairy waste cycle and the poultry cooling recycle, illustrate the need to demonstrate that recycled systems can yield an improvement in the performance of the industrial process, i.e. lower bacteria counts. However, more studies are needed to develop an understanding of system reliability and consequences of system failure.

Very little is known of the impact of organics in recycled wastes, principally because experience in recycling wastes containing organics is scanty. The Versar[10] evaluation of the published literature in the reuse/recycle area uncovered only one published work on the removal of organics from reused process water. Hence studies are needed by industry to determine the impact on product quality of organics in process waters. It may be found that in many cases the impact is negligible and recycled water quality may require less treatment than previously thought. Much is known about the removal of organics from wastewater but little is known about the need to do so.

Future application of adsorption techniques will inevitably increase as new strategies for recycling of industrial wastewater, recovery of valuable constituents and reduction in discharge of organic substances are developed.

Future applications of recycling will involve analysis of manufacturing processes and specification of recycling strategy for the individual process or plant. The objective will be to develop a comprehensive plan to reduce discharge of pollutants. Existing wastewater treatment technology will be used only to the extent that it fits into the plan.

Table 7 shows the results of one analysis of industrial recycling.[11] For this situation, a generalized representation, recycling was slightly less costly than the current practice. A more detailed analysis would also take the account accelerated-depreciation accounting, tax incentives, or other devices available to industry that favor selection of recycling. One research need involves determination of ways economic factors influence the decision to implement a recycling program.

An example of a potentially new technology is the use of conventional biological systems using genetically modified bacteria capable of degrading so-called "nonbiodegradable" wastes containing organic substances. Battelle Columbus Laboratories recently announced research efforts using bacteria to decompose toxic chemicals and pollutants such as DDT.[12]

The unit separation processes discussed in the previous section will all gain more widespread use in recycling strategies. However, much research is needed to optimize these processes for specific wastes. Concurrently, efforts must be made to reduce the amount of energy needed to achieve the required levels of treatment. This may involve modifications such as the use of both active and passive solar energy or the use of low-pressure waste steam to maintain optimum temperatures in biological treatment units to accelerate the rate of bio-oxidation of organics. Industry can use heat in this manner more easily than can municipalities.

Table 6. Comparison of Total Bacterial Counts of Dairy Equipment Cleaned with Recycled and with Conventional Sanitary Solutions.

	Arithmetic Mean of Bacterial Counts (no./mL) of 68 Samples	
Sampling Sites	Conventional Side	Recycled System
Random teat cup	2,500	6,400
2nd random teat cup	990	2,800
Receiver jar float	210,000	190,000
Pipeline joint	55	620
Final rinse water	19,000	24,000

Table 7. Cost Comparison of System Using Various Degrees of Recycled Wastewater.*

	100% to Sewer 0% to Recycle	40% to Sewer 60% Recycle	10% to Sewer 90% Recycle
Metals removal	$ 80	$ 80	$ 80
Wastewater treatment	70	1,810	1,910
In-plant modifications for recycle	0	120	150
Water charges	490	240	50
Sewer charges	2,000	700	140
TOTAL	$ 2,640	$ 2,950	$ 2,330

*Costs in $1,000's over a 10-yr period. Derived from Reference 11.

The extent to which energy can be conserved will significantly influence the economics of industrial recycling. Industry uses over two-thirds of its water supply for cooling needs. Methods of conserving energy used in cooling or of minimizing cooling requirements will attract increased research efforts. One promising alternative is simply to cool water only to the level actually required through the use of sophisticated instrumentation. Presently, cooling is often in excess of requirements. Cooling water additives are available to minimize organic fouling, or corrosion promoted by deposits of organic substances in the water.

In summary, research needs for recycling are not limited to technology-related problems. Economic, energy, institutional, and other factors will need closer scrutiny in order to increase the number of recycling facilities and their magnitude.

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MANAGEMENT OF ORGANIC RESIDUALS SEPARATED FROM INDUSTRIAL WASTES

C. Lue-Hing, T.B.S. Prakasam and D. Zenz

INTRODUCTION

A significant development in the strengthening of the control of water pollution in the United States was made in 1970 by consolidating various pollution control agencies spread throughout the Federal Executive Branch into one organization viz. the United States Environmental Protection Agency. The passage of the Federal Water Pollution Control Act in 1972, the Safe Drinking Water Act in 1974, the Toxic Substances Control Act (TSCA) in 1975, the Resource Conservation and Recovery Act (RCRA), in 1976, and the Clean Water Act in 1977 reflected the nation's determination to control pollution. While the Federal Water Pollution Control Act and its amendments seek to remove pollutants from wastewater, the RCRA, and to a minor extent TSCA, provide measures for the regulation and the ultimate disposal of solid wastes and the residuals separated from wastewater streams. In this chapter, some salient aspects of RCRA and a state-of-art of the treatment and disposal of organic residuals, particularly those which are hazardous and are separated from industrial wastes are discussed.

Resource Conservation and Recovery Act

The two basic objectives of RCRA are (1) protection of public health and environment, and (2) conservation of natural resources. To comply with RCRA regulations, the generators of hazardous wastes are required to keep records, insure

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proper packaging and labeling of wastes shipped off-site, and prepare a transport manifest document for each shipment describing content, amount, and destination. Although generators of hazardous wastes do not need permits, the RCRA regulations place considerable responsibility on them. They must determine whether their waste is hazardous and comply with RCRA regulations covering every step in waste storage, treatment and ultimate disposal including collecting information on the quantities of the hazardous waste generated.

Methods for Determining Quantities of Waste Residuals

A reliable estimate of the quantities of waste residuals generated in varoius industrial categories would of course be extremely valuable in planning, implementing, and regulating the disposal of such residuals. Unfortunately, there has been a lack of information in this area for a long time. Only recently, with the enactment of RCRA, has a concerted effort been initiated at the national, state, and local levels to obtain reliable estimates. However, the Illinois Environmental Protection Agency and the Metropolitan Sanitary District of Greater Chicago (MSDGC) began implementing their manifest systems in 1979; a summary of data taken from the MSDGC sludge manifest report forms for the year 1979 is given in Table 1.

The data indicate that less than 1% of the industries violated the requirement for reporting their waste generation. The fats, oils and grease (FOG) wastes representing about 21 percent of the waste generated are included as organic residuals. Most of the industrial sludges generated within the MSDGC jurisdiction are disposed of in three landfills in the Chicago area.

State and National Hazardous Waste Quantities

In a recently published study by the Illinois Institute of Natural Resources[1], an attempt was made to compare the quantity of hazardous waste residuals produced in Illinois with that generated nationwide as derived from various estimates. In arriving at these estimates, the Institute made two basic assumptions: (1) Illinois contributes 7% of the waste generated in USA, and (2) 10% of the total industrial waste produced is hazardous. No estimate of the organic fraction of the waste is given in the Institute's summary. Assuming that 60% of the total solids contained in hazardous waste streams is organic in composition, Table 2 presents an estimate of the total quantity of hazardous wastes and its organic component generated annually by industry.

The USEPA has estimated that the wastewater sludges generated by 14 major industries (petroleum refining, waste oil re-refining, organic chemicals, pesticides, explosives, inorganic chemicals, paint and allied products, pharmaceuticals, primary metals smelting and refining, textile dyeing and finishing, leather tanning, electronic components, rubber and plastics, electroplating) would increase from 22.7 x 10^6 tons/yr in 1977 to 42.8 x 10^6 tons/yr in 1978. Assuming as before, that 7 percent of this would represent the quantity produced by industries in Illinois, the total amount of wastewater sludges in Illinois would be 1.94 x 10^6 tons in 1977 and 3 x 10^6 tons in 1978.

WASTES FROM PRIMARY INDUSTRIES

Among the major industrial categories that generate waste residuals containing hazardous organics are those related to textiles, paint formulating, petroleum refining, and organic chemicals manufacturing (including pesticides and explosives).

Table 1. Data Extracted from the Metropolitan Sanitary District of Greater Chicago's Sludge Manifest Reporting System for February - December, 1979

(a) Number of manifest forms returned by industry	14,145
(b) Number of violations*	117
(c) % Violations	< 1

Type of Waste	Total Pounds
Metal/cyanide bearing wastes	161,800,000
Acid/alkali wastes	71,600,000
Fats, oils and grease wastes (FOG)	109,500,000
"Other" wastes	169,400,000
Total	512,300,000

*Violation means failure to return a manifest form.

Textile Industry

There are seven categories of plants in this industrial sector: (1) wool scouring, (2) wool fabric dyeing and finishing, (3) Greige goods (which employ dry operations like knitting and weaving and hence generate no hazardous wastes), (4) woven fabric dyeing and finishing, (5) knit fabric dyeing and finishing, (6) carpet dyeing and finishing, and (7) yarn and stock dyeing and finishing.[2]

About 69% of the plants are engaged in woven or knit dyeing and finishing operations. This industrial sector collectively produces 5.3 millions metric tons of product/year.

Textile waste streams contain hazardous toxic organics. Basic dyes, some acid dyes, and some dispersed dyes have been shown to be toxic to fish and hence are potentially hazardous when discharged in wastes. Some of the dyes may degrade in an anaerobic environment such as in landfills, and may produce a leachate of carcinogenic metabolites. Other organics that are most likely to be hazardous are dye carriers, solvents, and chemical finishes that find their way into textile waste streams. Dye carriers include biphenyl, butyl benzoate, methyl salicilate, trichlorobenzene, perchloroethylene, and other chlorinated aromatics. Some of these dye carriers are known to be non-biodegradable in activated sludge treatment systems. Biphenyl, toluene, and naphthalene are known to be toxic to activated sludge biota. Chlorinated organics which are hazardous compounds are reported to be present in various textile mill residuals.

The estimated quantity of waste residuals generated for the entire textile industry along with the quantities of potentially hazardous dye and chemical container wastes for the years 1974, 1977 and 1983 are given in Table 3. The estimated quantities of potentially hazardous wastewater treatment sludges are given in Table 4.[2]

The suspended solids concentration of sludges originating in the different types of textile mills is highly variable. Hence, the toxic organics associated with these solids may also be highly variable. A concentration as low as 0.008% suspended solids was reported for wool fabric dyeing and finishing sludges, whereas about 9.8 percent suspended solids was reported for wool scouring waste sludges.

Although a complete analysis of the organics and their concentration in sludges is not available, a range of 0.11 to 64.7 mg of chlorinated organics/kg of sludges generated from different types of textile mill sludges was observed.[2]

Table 2. Estimates of Total Solid and Hazardous Industrial Waste Generated and Organics Contained in it in USA and the State of Illinois (10^6 tons/yr)

	USA			Illinois		
Source*	Total	Hazardous	Organics	Total	Hazardous	Organics
Michael Rapps	300-500	30-50	18-30	21-35	21-3.5	1.26-2.1
A.D. Little Inc.	379	37.9	22.7	26.5	2.65	1.59
Booze-Allen Applied Research Inc.	283	28.3	17	19.8	1.98	1.2
Stephen James	506	50.6	30.4	35.4	3.54	2.12
USEPA 1977 Estimates	413	41.3	24.8	28.9	2.89	1.73
Robert S. Glaubinger	300-450	18-27	18-27	21-31.5	2.1-3.15	1.26-1.89

* Complete citation of the source is listed in Reference 1.

Assumptions made in the computation:

(1) 10% of the total waste is hazardous.
(2) Illinois generates 7% of the nation's waste.
(3) 60% of the hazardous waste is organic in nature.

Table 3. Estimated Quantities of Waste Residuals Generated in the Textile Industry (dry kkg/yr)[2]

Type	1974	1977	1983
(1) Total waste	310,000	336,000	534,000
(2) a. Potentially hazardous dye and chemical container wastes	10,000	10,400	12,300
b. Hazardous constituents	123	130	154

Potentially hazardous wastes and sludges from the textile industry originate from process operations and from wastewater treatment plants. All segments of the textile industry except the Griege goods category produce wastewater sludges that contain toxic organics. Wastewater from the textile industry plants is processed by the industry itself on-site or is discharged to the sewer for treatment by a municipality. Wastewater treatment sludges arise primarily from dyeing and finishing mills. Sludges generated in activated sludge plants and lagoons concentrate heavy metals and potentially hazardous organics, such as chlorinated organics and non-biodegradable dyestuffs.

While process wastes can be reduced or eliminated through good housekeeping and waste segregation, this is not the case for wastewater treatment sludges. It is also not possible to predict the degree of hazard associated with wastewater treatment sludges, although reasonably good estimates of process wastes can be made based on production schedules, quantities of raw materials used, and inventories of materials expended in the process.

Sludges are for the most part retained or stored in wastewater treatment systems. Sludge generated in aerobic treatment systems such as lagoons and activated sludge units is permitted to build up in the system to a maximum level at which time other holding basins become necessary. In some textile plants, the sludge is disposed on-site without taking advantage of its fertilizer value, whereas in others it is used in irrigation to grow crops.

An estimate of the number of textile plants and the level of technology they employ for disposing of waste treatment plant sludges is given in Table 5.

While a few textile mills incinerate their wastes, it is not a common practice in the industry because disposal of ash is a problem and air pollution may result.

In addition to the typical process wastes and wastewater treatment sludges generated by the textile industry, other atypical wastes are also generated. These are listed in Table 6 with the expected quantities of wastes generated and the technology for their disposal. As can be seen, these wastes are primarily solvents. Unlike the toxicity of wastewater treatment sludges, the hazard associated with these atypical wastes lies in their flammability. These wastes are adequately disposed of by recovery and incineration. Atypical waste such as lint contaminated with dye is disposed of by landfill. Indiscriminate use of landfills does pose a hazard, but this can be alleviated by disposing of the waste in an approved and secured landfill or by incineration.[2]

Plastic Materials and Synthetics Industry

This industrial category (Standard Industrial Classification Code 282), includes plants that produce (1) plastic materials and resins, (2) synthetic rubber, (3) cellulosic man-made fibers, and (4) organic fibers that are non-cellulosic. These industries in 1972 produced about $16 billion worth of goods.[3]

Table 4. Total Quantity of Potentially Hazardous Wastewater Treatment Sludges, dry kkg/yr Generated in the Textile Industry[2]

Type	1974		1977		1983
	Retained* Sludges	Wasted Sludges	Retained* Sludges	Wasted Sludges	All Sludges
Total	29.9	38,400	29	39,100	167×10^{3}
Total chlorinated organics	756.6×10^{-6}	230×10^{-3}	790×10^{-6}	240×10^{-3}	2500×10^{-3}
Dye stuff	1117×10^{-3}	645	1150×10^{-3}	680	7,700
Total hazardous constituents	1321×10^{-3}	900	1350×10^{-3}	940	9,200

*Sludge retained or accumulated in the waste treatment system.

Table 5. Number of Plants Employing Current and Best Technology for the Disposal of Waste Treatment Plant Sludges in the Textile Industry*[2]

	Current Technology		Best Technology	
Category	Retention of Sludge	Land Disposal of Wasted Sludge	Line-Pond Retention of Sludges	Approved Landfill of Wasted Sludge
1. Wool scouring	8 (50)	8 (100)	5 (67)	0 (0)
2. Wool fabric dyeing and finishing	39 (35)	0 (0)	0 (0)	0 (0)
3. Woven fabric dyeing and finishing	208 (32)	86 (41)	0 (0)	0 (0)
4. Knit fabric dyeing and finishing	125 (17)	0 (0)	15 (12)	15 (12)
5. Carpet dyeing and finishing	43 (30)	0 (0)	0 (0)	0 (0)
6. Yarn and stock dyeing and finishing	65 (19)	0 (0)	0 (0)	0 (0)

*Values in parenthesis are percentages and are based on the total number of plants visited.

Table 6. Atypical Waste Residuals Generated in the Textile Industry[2]

Category	Waste	Waste Quantity kg/kkg of Product	Disposal Technology
1. Wool fabric dyeing and finishing	Still bottoms from recovery of dry cleaning chlorinated solvents	5	Present-sealed in drums and sent to land fills or dumps Future-reclamation/or incineration
2. Woven fabric dyeing and finishing	Hydrocarbon solvent and sludges	50	Present-landfilling Future-reclaiming/incineration
3. Woven fabric dyeing and finishing	Finishing sludges containing adhesives, silicones, and solvents	333	Present-landfilling Future-reclaiming/incineration
4. Knit fabric dyeing and finishing	Acetone recovery still bottoms	63	Present-incineration, environmentally adequate
5. Knit fabric dyeing and finishing	Perchloroethylene still bottoms	10	Present-reclaimed by contractor, environmentally adequate
6. Carpet dyeing and finishing	Lint with wet dye	12	Present-landfilling along with trash Future-includes washing, approved landfilling or incineration
7. Yarn and stock dyeing and finishing	Solvent resin slurries	0.09	Present-sealed in drums and stored on site Future-reclamation, approved landfilling or incineration

The two major processes used in this industry are polymerization of simple molecules to form a polymer, and spinning of the product polymer to form a fiber. In the production of polymers several chemicals are used. In addition to the monomers, compounds characterized as modifiers, plasticizers, chemical additives, dyes and pigments, and processing chemicals are used to obtain polymers of desired properties.

The following types of wastes are generated from the polymerization process: (1) off-grade products, resulting from upsets in production, mechanical failures, etc., (2) still bottoms resulting from monomer or solvent recovery and consisting of short chain polymerized material and other degradable compounds of solvent and product, (3) spent adsorbents and filters used to remove water for conditioning the product, (4) spent catalysts which in some instances are discharged into the wastewater treatment plant and thus become a part of the sludge, (5) waste oils, a part of which may find their way into the sewer, the remainder being collected in drums, and (6) wastewater treatment plant sludges.[3]

The synthetics manufacturing plants usually provide wastewater treatment. The sludges generated in polymerization process alone are minor in quantity. These treatment plants may include a pretreatment step involving pH adjustment and addition of coagulants prior to clarification. Secondary treatment may be provided in which compounds such as alcohols discharged from the polymerization process may be oxidized to form additional sludge.

The waste generation factors for the non-olefinic and olefinic polymer industry were estimated for various products and are given in Table 7.[3]

In addition to the wastes generated in the manufacturing of the textile products, others are generated in the spinning operations; for example, in the spinning of acrylics and rayon, considerable amounts of wastewater sludges are generated in addition to other wastes such as off-grade products, still bottoms, and oils. The wastewater sludge associated with the spinning of acrylics and rayon amounted to 20% of the product. In the rayon industry, difficulties are experienced in meeting prescribed effluent guidelines and as a result several rayon plants have been closed. In addition, the wastewater sludges have been characterized as hazardous. The quantity of potentially hazardous waste generated in this industry was estimated at 5660 kkg/yr on a wet basis. However, most of the hazardous constituents in sludges are metals, primarily zinc. Wastes from phenolic resin production are considered hazardous because of the presence of high concentrations of phenol. The concentration of organic material is highly variable, ranging from 5 to 15%, and includes both phenol and off-grade products. Similarly, wastes from amino-resin manufacture are considered hazardous because of the presence of formaldehyde and methanol.

The still bottoms generated in the production of ABS-SAN, polystyrene, polypropylene, polybutadiene, and neoprine are also considered potentially hazardous because of the presence of highly flammable solvents and may contain polycyclic aromatics. However, the aqueous still bottoms which are generally discharged to the wastewater treatment system do not pose any particular problem.

The total estimated quantity of potentially hazardous waste for the years 1974, 1977, and 1983 for the plastics and synthetics industry was reported to be 740,000; 896,000; and 1,156,000 kkg (wet), respectively.[3]

The largest contribution to the potentially hazardous wastes that are destined for land disposal is reported to be from plants producing polystyrene, phenolics and amino-resins and from the acrylic spinning process. The largest single contribution, however, is from the phenolics industry with an estimated 366,000 kkg of an aqueous solution of phenol and formaldehyde in the year 1974.

The disposal of wastes generated in the plastics and synthetics industry is presently carried by controlled incineration, landfilling, lagooning, and storage.

Two distinct types of hazardous waste streams are generated in the phenolics segment as indicated earlier. These are the low viscosity pumpable stream of phenol and/or formaldehyde waste stream and the semi-solid waste stream containing the

Table 7. Waste Generation Factors as Percent of Total Production in Various Polymer Production Categories[3]

Category	Off-grade Products (%)	Still Bottoms and Waste Oils (%)	Other (%)	Estimated Quantity of Potentially Hazardous Waste 1974 kkg/yr (wet)
Non-olefinic polymers				
Acrylic and modacrylics	0.2	0.7	—	278,000
Nylon 6 (polyamide)	0.02	NA	—	
Nylon 6,6 (polyamide)	0.3	NA	Wastewater sludge and spent filter cake. 0.3	
Polyester resin	3.	0.01	Terephthalic acid. 0.1	
Phenolic resin	0.8	3.8	Wastewater sludge. 6.0	368,000
Amino formaldehyde	1.0	1.2	Filter cake. 0.24	20,735
Coumarone-indene	NA	NA	Spent clay. 3.6 (40% organic residue)	5,328
Alkyd resin	0.1	NA	Sweepings 0.01	32
Silicone products	5.4	5.8	Spent adsorbent & scrap. 3.3	
Olefinic polymers				
Styrene butadiene	2.5	1.15	Wastewater sludge: 1.3	18,440
Rubber polyethylene				
Low density	1.0	1.0	—	
High density	0.3	0.05	Spent adsorbent & catalyst <0.1	
Vinyl chloride	2	NA	Wastewater sludge 1.1	10,260
Vinyl acetate	1	0.1	NA	
ABS-SAN*	2	0.5	Wastewater sludge 1.0	2,200
Polypropylene	0.5	1.0	Wastewater sludge 0.2 (dry)	4,940

* ABS-SAN: Acrylonitrile butadiene styrene, SAN: Styrene acrylonitrile

oligomers and phenol. The liquid stream is incinerated on-site by supplementing it with waste solvent stored on-site from other industries. The semi-solid waste stream is lagooned, but this is not a satisfactory method of disposal. Other wastes that are incinerated either on-site or off-site by a contractor consist of amino-resins, polyester catalyst waste stream and still bottoms. The incineration of still bottoms results in practically no ash. This is environmentally safe and also economical because of the high energy value of the still bottoms.

Paint Formulating Industry

The major products of the paint formulating industry (SIC 2851) are (1) trade sales paints, which are primarily exterior and interior paints for buildings and structures, and (2) industrial sales paints for application to products such as cars, aircraft, furniture, etc. In addition, varnishes and lacquers are also manufactured by this industry. A survey showed that there are 1374 plants in the USA manufacturing paint; the paint sales were estimated at \$1871 x 10^6 in 1974. Another segment of this industry manufactures allied products such as putty, caulking compounds, sealants, stripping compounds, and paint thinners.[4]

The rinsing and washing operations of mixing tanks and filling equipment contribute the bulk of wastewater from this industry. Other sources such as floors, spill cleaning operations, laboratory sinks, air pollution equipment using water rinses, raw material tanks, and boiler and cooling water blow-down also contribute wastewater. Generally, sanitary waste and non-contact cooling water are segregated and discharged to the municipal sewers. Practices promoting a reduction in the amount of water used in the manufacturing process and reuse of the wastewater are widely used to reduce the amount of wastewater discharged.

According to an EPA report[4], the paint industry generates annually an estimated 5.7 million liters (1.5 million gallons) of process wastewater. About half of the wastewater (2.8 million liters) is discharged whereas the other half is reused in the plants, evaporated or disposed of in sealed drums.

Of the 22 plants surveyed in the above report, 17 treated their wastewaters by means of a batch physico-chemical treatment system involving coagulation, mixing, and settling. Three other plants used a continuous flow physico-chemical treatment system, whereas the other two used neutralization followed by gravity settling for treating their wastewaters.

Biological treatment has been reported to be applicable for latex-bearing wastes. Pretreatment is required to remove the heavy solids prior to subjecting the wastewater to biological waste treatment. Although activated sludge and trickling filters can be used for processing latex wastewaters, aerated lagoons predominate in the industry.

The characteristics of the sludge separated from the wastewater with particular reference to the organics contained are presented in Table 8.

A study by EPA's solid waste management branch in 1976 estimated that the paint manufacturing industry generated 436,000 metric tons of waste in 1974 (wet basis). Of this, 105,000 tons were included in the category of potentially hazardous materials. This study has also found that most of these wastes are disposed of in off-site landfills.[4]

It is also estimated that about 420,000 liters/day of sludge would be produced if the entire volume of 2.8 million liters of waste that is currently discharged by the industry is processed by physico-chemical treatment. This quantity of sludge would amount to 15% of the waste volume. Based on the average concentration of organic constituents listed in Table 8, the toxic organic load would be about 72 kg/day (159 lb/day); the major contribution to this load being methylene chloride (63%), toluene (23%), and ethyl benzene (7%). If in-plant controls for wastewater volume reduction, such as wastewater recycle and improved tank cleaning and rinsing procedures are employed, the quantities of sludge produced will be reduced. Thus, it is estimated

Table 8. Concentration of Toxic Organic Pollutants in Sludge from Paint Formulating Industry[4]

Organic Compound	Average Concentration μg/L	Number of Samples Having about 10 μg/L
Benzene	414	4/8
Carbon tetrachloride	<10	—
Chlorobenzene	176	2/9
1,2-Dichloroethane	17	1/9
1,1,1-Trichloroethane	866	4/9
1,1,2,2 Tetrachloroethane	13	1/9
2,4,6 Trichlorophenol	<10	—
Chloroform	920	2/9
2,4 Dimethyl phenol	<10	—
Ethyl benzene	14,277	8/9
Methylene chloride	120,201	8/9
Napthalene	366	3/9
2,4 Dinitrophenol	18	1/9
Pentachlorophenol	346	4/9
Phenols	325	3/9
Total phenols	552	30/37
Di (2-ethylhexyl) phthalate	455	6/9
Butyl benzyl phthalate	10,410	4/9
Di-N-butyl phthalate	3,622	4/9
Diethyl phthalate	370	3/9
Dimethyl phthalate	<10	—
Anthracene	<210	1/9
Pyrene	<10	—
Tetrachloroethylene	2142	4/9
Toluene	44,740	8/9
Trichloroethylene	<39	2/9
Aldrin	<10	—
β-endosulfan	<10	—

(4/8 means four samples out of a total of eight samples analyzed, etc.)

that an 80% reduction in wastewater discharged would result in a sludge quantity of 3% of the wastewater volume discharged. For the entire volume of wastewater generated in the industry, the total hazardous waste produced was estimated between 150,000 to 300,000 metric tons/yr. Also, the toxic organic pollutant loading would amount to 140 kg/day. Although procedures are employed to reduce wastewater flows, the total organic pollutant load will not significantly affect the quantity of toxic pollutants to be discharged. Nevertheless, the costs for contract hauling would be lowered because of the reduction in the volume of the wastes.

An assessment study conducted by WAPORA, Inc., for EPA on the industrial waste disposal practices in the paint and allied products industry reported that landfilling of the waste residuals was by far the single largest practice employed in this industry. The quantities of various hazardous waste residuals generated in this industry and their mode of disposal are summarized in Table 9.[4]

Petroleum Refining Industry

A report prepared by Jacobs Engineering Company, Pasadena, California, in 1974 for the EPA, states that there are 247 refineries (SIC 3111) in the United States.[5]

Table 9. Quantities of Hazardous Waste Residuals and Mode of Disposal in Paints and Coatings Industry (SIC 285)[4]

Waste Type	Total Quantity of Hazardous Waste Tonnes/Year, 1977 (Wet-basis)	Disposal Methods- (Number of Plants, 1972 Basis: 1544 Plants)		Technology		
		Incineration	Landfill[a]	Level I	Level II	Level III
Raw material Packaging wastes[b]	2000	55	1540	Off-site landfill	Same as Level I	Segregation of waste in bags and incineration, ash disposal in secured landfill.
Wastewater sludge	2300	—	1120	Hauled from off-site land disposal	Same as Level I	Sedimentation, Dewatering, followed by disposal in a secured landfill.
Spills and spoiled batches	11800	—	1540	Off-site landfill	Same as Level I	Incineration followed by ash disposal in a secured landfill.
Waste organic Cleaning solvent	94800	25	1000	Off-site landfill in drums	Off-site solvent reprocessing, incineration of still bottoms, ash disposal in landfill.	Same as Level II
Dust from air pollution control equipment	1800	—	1000	Off-site landfill, in drums	Reuse of waste as a pigment extender in low-grade paint	(1) Same as Level II (2) Secured landfill disposal.

a. "Landfill" may include open dumps, sanitary landfills, secured landfills, etc.
b. Plant Total for disposal methods adds to more than the total number of plants since some plants use two or more disposal methods.
c. Level I means prevalent technology, Level II best available technology, Level III technology necessary to meet strict health and environmental standards.

However, the Development Document for Proposed Effluent Limitation Guidelines for the Petroleum Refining Point Source Category, identified 285 refineries in the USA and its territorial possessions.[6] The Jacobs Engineering Company report gives the following distribution for the refineries producing different products: (1) residual oil, 227; (2) distilled fuel oil, 226; (3) motor gasoline, 212; (4) unfinished oil, 172; (5) kerosene, including range oil, 154; (6) coke, 148; (7) wax products, 60; and (8) lubricating grease, 18.

Refineries can be classified into 4 categories depending on the refining processes they incorporate. They are given in Table 10, along with the types of residuals they generate.

Several factors do influence the composition and quantity of specific residual waste streams. Among the more important of these factors are the following: (1) the composition of raw crude used, (2) raw water employed, (3) degree of pretreatment of water, (4) process used for refining, (5) metallurgy of various unit processes employed, (6) plant house keeping, (7) air pollution control and water pollution control technologies employed, and (8) refining plant capacity.

The characteristics of sludge generated in the wastewater treatment processes are influenced by composition of the wastewater processed, type of biological treatment and primary treatment employed, and sludge conditioning and concentration techniques used.

Numerous organics were reported to be discharged in petroleum refinery wastes.[5,6] Several hazardous organics were identified in petroleum refinery wastes by examination of the "oil" fraction. Polynuclear aromatics, e.g., benz-a-pyrene, and phenols are integral parts of residuals separated from various refinery waste streams. The 16 types of residuals generated as indicated in Table 10, have highly variable solids concentrations within the range of 1-100%. Wastewater treatment sludges for example were reported to have a solids concentration of 5 to 44%. The concentrations of oil, phenols, and benz-a-pyrene were also highly variable in these sludges, averaging 2800 mg/kg, 4.5 mg/kg, and 0.003 mg/kg, respectively, in waste biological sludge. In addition to these hazardous constituents, several heavy metals are also found in these sludge streams.

In an inter-laboratory comparison of the concentrations of the above constituents made by Jacobs Engineering and the refineries, a wide variation in the observed concentrations was noted. This suggests a need for scrutiny and standardization of the analytical methodology involved.

The spent lime sludge stream contributes the highest amount of sludge and amounts to about 50% or higher of the total amount of sludge produced in any of the types of refineries. In contrast, the wastewater treatment sludges amount to about 2% of the total residual waste solids produced in a refinery.

The quantities of some of the hazardous substances in wastewater treatment sludges and in all sludges generated in the petroleum refinery industry are given in Table 11. For comparison, the expected quantities of potentially hazardous wastes as a result of water pollution regulations for the years 1974, 1977 and 1983 are given in this table. As can be seen from these data, the hazardous constitutent of these sludges is essentially oil.

A reduction in the total quantity of hazardous constituents is expected in 1983 because of increased oil recovery, reduced use of lead and metals such as chromium and zinc in cooling towers. Since additional refineries are expected to use secondary biological waste treatment, the quantity of wastewater treatment sludges is likely to increase.

Reported studies on the fate of organics, particularly those of hazardous organics in biological waste treatment systems are relatively sparse. However, when petroleum refinery wastewaters are discharged into a publicly owned treatment works (POTW), they do exert an influence on the characteristics of the secondary effluent and sludge generated. Data reported from one study, in which the fate of organics discharged into a POTW from 5 refineries was investigated, showed the

Table 10. Types of Refineries and the Wastes They Generate[5]

Refinery Type	Type of Processes Included	Wastes Generated
I	Crude Vacuum distillation; LP recovery; Hydrotreating; Reforming; Alkylation; Isomerization; Visbreaking.	1) slop oil emulsion solids, 2) once-through cooling sludge, 3) Spent lime from boiler feed water treatment, 4) exchange bundle cleaning sludge, 5) API separator sludge, 6) dissolved air flotation float (DAF), 7) kerosene filter clays, 8) crude tank bottoms, 9) leaded tank bottoms, 10) non-leaded tank bottoms, 11) neutralized HF alkylation sludges, 12) storm water silt, and 13) waste bio sludge.
II	All processes included in Type I in addition to fluid catcracking and hydroflowing.	All of above and 14) FCC catalyst fines
III	All processes included in Type II in addition to fluid or delayed coking.	All in II above and 15) coke fines.
IV	All processes included in Type III in addition to lube oil and petrochemical operations.	All in III above and 16) lube oil filter clays.

Table 11. Production of Potentially Hazardous Constituents in Wastewater Treatment Sludges and all Waste Residuals from Petroleum Refining Industry in 1974, 1977, 1983 (tons, dry wt.)[5]

Parameter	Wastewater Treatment Sludges 1974	All Sludges		
		1974	1977	1983
Phenols	0.4	5.41	6.34	7.28
Benz-a-pyrene	0.0002	0.003	0.113	0.153
Oil	228	109,000	110,000	112,000
Total Weight	10,800	625,000	715,000	811,000
% H_2O	87			
Total Weight of Hazardous Components	36.7*	110,000	117,000	114,000

*Oil is not included.

profiles of concentrations of various organics in the refinery effluent, POTW influent, secondary effluent, and sludge.[5] These data are presented in Table 12. It can be seen that many of the compounds listed did survive the treatment process and appeared in the secondary effluent. Also, the oil and grease fraction was concentrated in the sludge and was not completely degraded in the digestion process. Results of profiling of another POTW into which wastewater from only one refinery was discharged indicated that most of the organics monitored were removed and the effluent contained at best traces of these compounds. However, oil and grease, ethyl benzene, toluene, napthalene, butyl benzyl phthalate, phenol, and diethylphthalate were detected in significant concentrations in primary sludge. Oil and grease and phenol were also found in significant amounts in secondary sludge.

The prevalent methodology for the disposal of petroleum refining sludges consists of (1) landfilling, (2) lagooning, (3) incineration, and (4) land spreading. Estimates of the on-site and off-site disposal of petroleum refinery sludges using these procedures for the years 1973 and 1983 are given in Table 13.

The figures given in Table 13 for 1983 which are projected by Jacobs Engineering, Pasadena, California, show a very significant decrease in off-site landfilling and lagooning practices with a simultaneous increase in the on-site disposal practices. This trend is a reflection of the emerging environmental regulations. Disposal of petroleum wastes in municipal landfills is being gradually eliminated. The current trend in the industry is to achieve self sufficiency in their disposal practices.

In land disposal of refinery sludge, the application rate varies from 1" to 2" in northwestern USA to as much as 3" to 4" in the warmer southwestern USA. The degradable fraction of the oil is metabolized by the soil microorganisms. Depending on the application rate, agronomic practices, and environmental conditions, the degradation may take about 1 to 6 months.[5]

The Arthur D. Little Company reported results of a land farming study involving the application of a refinery sludge contained in holding ponds.[7] This sludge contained 13% solids, 25% oil and 62% water, with an extractable organic matter concentration of 1100 mg/L (composed as follows: non-volatile aliphatic hydrocarbons, 41%; volatile aliphatic hydrocarbons, 39%; non-volatile aromatic hydrocarbons, 10%; volatile aromatic hydrocarbons, 3%; and non-volatile polar organics, 7%). Approximately 68,000 gallons of this sludge was applied on 1.7 acres and allowed to dry over a period of several weeks. Then it was rototilled to a depth of 5-6". Samples taken at a depth of 0-6" and 6-12" after such a treatment still contained extractable organics at a concentration of 3,000 mg/kg and 520 mg/kg in comparison to the control area concentration of 140 mg/kg and 89 mg/kg. Thus, complete degradation was not achieved. It was also observed that there was a shift towards polar organics, and a substantial quantity of aliphatic and aromatic hydrocarbons had not undergone degradation. Non-volatile aliphatics appeared to have a higher rate of degradation than non-volatile aromatics. Also, the volatile aliphatic and aromatic hydrocarbons appeared to have been preferentially lost from the application site. The cost in disposal at this site was estimated to be 37¢/gallon of waste treated which includes both capital and operating expenses.

Lagooning of sludge as a disposal method is more of a convenience rather than one of an environmentally accepted practice. This practice is being looked down upon by several states and is permitted only as a temporary measure.

The disposal of sludge containing organic lead poses a hazard particularly because of health considerations. The disposal of organic lead sludges involves placing the settled sludge into a diked area and allowing it to weather and degrade. Alternatively, it is transported to a site in the refinery and rototilled into the soil.

Incineration is used in some refineries to dispose of dissolved air flotation sludge, slop oil emulsion solids, wastewater treatment sludges, and API separator sludge. But, due to the increase in energy costs, need to dispose of ash in an environmentally safe way, and pressure to recover more oil from sludges, incineration will become more costly and unfeasible in the future.

Table 12. Concentration of Organics in Influent, Effluent, and Sludges from a POTW Receiving Refinery Wastewater+5

Parameter	Effluents From Refineries	Primary Effluent	Final Effluent	Primary Sludge	Digested Sludge	Centrate	Filter Cake μg/kg
Benzene	T-1200	27-71	38-62	40	17	ND	6
1,1,1-Trichloroethane	ND-15	95-252	97-364	ND-50	ND	ND	ND
Chloroform	ND-21	13-111	12-19	ND-13	ND	ND	ND
Ethyl Benzene	ND-18,000	41-51	48-53	70-150	55-75	15	15-25
Toluene	ND-48,000	72-197	ND-80	260	75	65	8
2,4-Dimethylphenol	ND-9300	ND-750	180-740	ND	ND	ND	ND
Phenol	ND-14,000	210-840	160-660	ND-470	1300-1900	4600-7300	ND
Naphthalene	ND-425	23-35		70-305	125-565	340-480	ND-90
Anthracene	ND-81	ND-T	ND-T	ND-T	ND-T	ND-T	ND-T
Phenanthrene	ND-81	ND-T	ND-T	ND-T	ND-T	ND-T	ND-T
Oil & Grease mg/L	3.1-774	82-113	29.3-34.7	3,100-6,580	2,420-2,640	1,660-1,680	NA

+ 5 Refineries discharged into this POTW in California. All values are μg/L, unless otherwise indicated.
ND: Not Detected, T: Trace

Table 13. Percent Estimates of Refinery Sludge Disposal Methodologies for 1973 and 1983[5]

Disposal Procedure	1973 Onsite (%)	1973 Offsite (%)	1983 Onsite (%)	1983 Offsite (%)
Landfilling	16.8	34.3	24	20
Lagooning	18.3	21.4	12	7
Incineration	0.8	0	3	0
Landspreading	8.4	0	34	0
Total	44.3	55.7	73	27

Concentration techniques usually used for increasing the solids concentration of municipal sludges may also be used for some petroleum refinery sludges. For example, sludge streams such as crude tank bottoms, and API separator bottom sludges can be concentrated by dewatering with polyelectrolytes and by alternate freeze-thaw cycles where climate permits. The concentrated sludges may then be disposed of on land.

Only in special cases are both liquid and solid wastes generated in petroleum refining industry processed by chemical fixation and disposed on land. Chemically inert precipitates are produced, for example, by the addition of chemical coagulants. In one patented process, solidification of about 20 million gallons of primarily lagooned API separator bottoms and crude tank bottoms was achieved by addition of substances such as cement. Such chemically fixed sludges had not produced a significant leachate problem.[8] The process has been reported to stabilize materials with as much as 38% solids; leaching of various ions is controlled by the amounts of silicates added. However, methods such as solidification and encapsulation of wastes in plastic or concrete are not widely used in the petroleum refining industry.

Composting of waste activated sludge and petroleum refinery sludges has been reported. However, it is not practiced on a large scale and its full scale application in this industry has yet to be proven.[9]

The prevalent technology for the disposal of sludges in this industry is mostly by landfilling. Leaded gasoline sludges are pumped into lagoons and allowed to dry. When drying is complete, the lagoon is covered. Landfilling of sludges as practiced currently is inadequate for the disposal of sludges from an environmental standpoint. However, the disposal of waste biological sludge is done in secured landfills and hence is considered to be adequate. Specification of an accepted level of technology for safeguarding health and environmental protection calls for landfilling in a secured area which is hydrogeologically safe.

Organic Chemicals Industry

About 87 million metric tons of products are estimated to be produced annually by industries manufacturing gum and wood chemicals, cyclic crudes and intermediates, industrial organic chemicals, pesticides and pesticide formulations, and explosives.[10] Waste residuals from these industries include solvents, acids and bases, sludges (heavy metal and paint), still and tank bottoms, oils, organic and inorganic toxic compounds, and waste treatment sludges.

The quantities of wastes produced from selected organic chemical and pesticide manufacturing plants along with the hazardous organic constituents contained in their wastes are presented in Table 14. The different levels of technology reflecting

Table 14. Quantities of Hazardous Components and Methods of Disposal of Residuals from Organic Chemicals Industry[10]

Product	Selected Waste Stream	Hazardous and Other Components	Quantity of Hazardous Components, metric tons/yr.	Total Waste Quantity metric tons/yr.	Technology		
					Level I	Level II	Level III
Perchloroethylene	Liquid heavy ends from purification column	Hexachlorobutadiene	8050	10,500	Deep well injection	Controlled incineration	Same as Level II
		Hexachlorobenzene	700				
		Chloroethane	350				
		Chlorobutadiene	350				
		Tars and Residues	700				
		Other compounds (Unknown)	350				
Nitrobenzene	Liquid still heavy ends	Nitrobenzene Heavyends	50	50	On-site Landfill	"	"
Chloromethane Solvents	Solid tails from solvent recovery system	Hexachlorobenzene	300	300	Contractor Landfill	"	"
		Crude Hexachlorobutadiene and other chlorinated paraffins	small				
Epichlorohydrin	Still bottoms	1,2,3-Trichloropropane	2783	3,975	On-site Storage	"	"
		Tetrachloropropyl-Ethers	557				
		Dichloropropanol	425				
		Epichlorohydrin	80				
		Chlorinated aliphatics and alcohols	130				
		Water and unidentified products	100				
Toluene Diisocyanate	Centrifuge residue sludge	Lower polyurethane polymers and tars	523	592	On-site Landfill	Controlled incineration	Same as Level II
		Waste isocyanates	16				
		$FeCl_3$	37				
		Unknown	16				
Vinyl Chloride	Still bottoms	Halogenated aliphatic	3780	3,800	Contractor	"	"

Mononer		Hydrocarbons Tars Inorganics	 5 15		incineration		
Acrylonitrile	Still bottoms	Higher nitriles & Polymers	160	160	Uncontrolled incineration	"	"
Maleic Anhydride	Sludge & Residue from distillation column	Maleic anhydride, Tars, Fumaric acid, and chromogenic compounds	333	333	Landfill	Secured Landfill	Secured Landfill
Lead Alkyls	Lead Sludge from settling basins	Organic lead compounds, & other organics Water & other inorganic salts	6000 24,000	30,000	Incineration	Controlled incineration	Same as Level II
Pesticides							
Aldrin	Area & Equipment Washdown	Aldrin Water & Dissolved Salts	29 288,971	289,000	Lined Pond	Same as Level I	Same as Level I
Atrazine	Scrubber spent alkali solution	Cyanuric acid insoluble Residue Water NaCl & NaOH	120 3,240 202,140 19,100	224,600	Deepwell Disposal	Same as Level I	Chemical Detoxification by ozonation and deepwell disposal
Parathion	Sulfur sludge from chlorinator	Sulfur & Organo phosphorus compound	2,300	2,300	Uncontrolled incineration	Secured Landfill	Same as Level II
Malathion	Filter cake solid (semi-solid)	Dimethyl Dithiophosphoric acid Toluene and insoluble reactor reactor products Filter lands	70 756 1,000	1,826	NaOH Treatment followed by approved site	Same as Level I	Same as Level I

a. Level I means prevalent technology, Level II best available technology, Level III technology necessary to meet strict health and environmental standards.

the current state-of-art and treatment that is acceptable and required for the disposal of residuals to maintain an adequate health standard (Levels II and III) are also given in this table.

Data reported for selected organic manufacturing plants indicated that only 24,325 metric tons of sludge originated from biological treatment processes and the remainder of about 420,000 metric tons of waste residual solids originated from other unit processes. Thus, it appears that only a small portion of the total sludge quantity in this industrial category is produced in wastewater treatment processes.

As it can be seen from Table 14, many of the waste residuals are recalcitrant and are contained in non-aqueous streams. Thus, their treatment and disposal are quite different from treatment and disposal of residuals separated from industrial wastewaters which are biodegradable. The major disposal technique for the disposal of many of these wastes is incineration (about 70% on a dry solids basis). However, disposal in approved landfill sites is also an accepted method of disposal for some wastes (about 15% on a dry solids basis). For the organic chemicals category, it should be noted that on a wet weight basis, disposal by deep well represents the most commonly employed method (about 64%) as presented in Table 15.

Explosives Industries

The explosives industry manufactures products such as (1) initiating agents and primers, (2) propellents of different kinds, (3) high explosives, (4) pyrotechnical incendiaries, (5) riot control agents, and (6) chemical warfare agents. The wastes containing hazardous organic compounds of importance include waste explosives, inerts contaminated with explosives, spent activated carbon resulting from processing aqueous wastes, red water from TNT production, organic solvents from propellent manufacture, and wastewaters containing RDX and HMX (high explosives). A characterization of these wastes and their hazardous constituents contained in each of these types of wastes is given in Table 16.

Waterborne wastes are also discharged from the explosives industry. These wastes may be processed by biological waste treatment and the sludge generated can be lagooned and disposed of on land.

The ultimate disposal of explosive industry waste residuals is carried out by (1) open burning on-site by a contractor, (2) detoxification followed by landfilling, (3) deep well disposal, and (4) storage in lagoons. Spray irrigation of ammunition wastes has been practiced in South Africa.[11] Open burning of explosive wastes is considered to be environmentally objectionable because of resulting air pollution problems it causes. Controlled incineration which has been developed recently appears to be promising. In a study in which six different incineration designs were evaluated the fluidized bed type of incinerator was judged to be the most promising system from the standpoint of low emission rates and operational cost.[12]

Food Industry

In addition to the organic residuals generated by the major industries listed above, significant quantities of organic sludges are produced by such industries as food processing and allied industries which generate sludges that can be considered as non-hazardous.

The amount of sludge to be disposed of ultimately depends on factors such as the character of wastewater, type of wastewater treatment process used, and sludge treatment applied.

Information on the total quantities of sludge produced from industrial wastes considered to be non-hazardous is meager, although estimates of waste generation factors for industries producing food, meat products, canned foods, and beverages have been reported.[11] These are usually expressed as the pounds of waste produced/1,000 pounds of product divided by the value added/1,000 pounds of

Table 15. Hazardous Waste Disposal Practices in the Organic Chemicals Industry[10]

Industrial Category	Type of Waste Residuals	Quanity/yr	Disposal Methods	Wet Wt Basis (%)	Dry Wt Basis (%)
Organic Chemicals (SCI 2861, 2865, 2869 except 28694 i.e., pesticides.)	All hazardous waste residuals from these categories	~10.3 million tons/yr wet basis, 1977	On-site landfilling	14.7	14.8
			Off-site landfilling	1.1	
			Controlled on-site incineration	6.8	21.7
			Uncontrolled on-site incineration	15.4	48.0
			On-site deep well	63.5	2.0
			Biological treatment lagoon	5.5	0.2
			Recovery	2.6	8.3
Pesticides SIC 28694 2879	Waste Pesticides, Pesticide contaminated items, waste-water, solvents, floor sweeping, etc.	~625,000 wet basis, 1977	On-site landfilling	28	
			Off-site incineration in privately owned incinerators	16	
			Storage in drums or open piles	13	
			Recovery	8	
			Undetermined landfill sites	12	
			Unknown	23	
Explosives SIC 2892 Private Industry	Blasting agents & Fixed high explosive waste	~5500 wet tons	Open-burning on-site		88.2
			Detoxification, followed by landfilling, deep well disposal, spray irrigation and lagooning		6
Government owned and contractor operated segment	Explosive wastes & explosive contaminated inert wastes	19,600 dry tons	Open burning		94.3
	Other hazardous wastes include spent a 4 carbon from aqueous waste processing, red water from TNT, purification, organic solvents from propellent manufacture, waste-waters containing dissolved and suspended RDX/HMR	240 dry tons	Landfill		58.3
			Openburning		37.5
			Sold		4
			Very little disposal in municipal plants		

Table 16. Characterization of Explosive Propellent and Warfare Material Wastes

Class	Hazardous Constituents in Wastes
Initiating Agents and Primers	Mercury fulminate, Lead azide, Lead styphnate, tetrazene, BPEHN
Propellents, Nitrocellulose based	Smokeless gunpowder, nitrocellulose, gelatinized nitrocellulose, rocket propellent (double base), ballistite, pyrocellulose, composition D-Z, nitroglycerin.
Propellents, composite/other	Rocket propellent TP-H-1011, Rocket propellent TP-H-1016, Rocket propellent ANB 3066 Ammonium perchlorate
High Explosives	Ammonium picrate, glycol dinitrate, picric acid, PETN, TNT, dynamite, compositions, A, B, B_2, C, RDX, HMX, Plastic explosives.
Riot Control Agents	Chlorcielophenone tear gas (N) Tear Gas irritant (CS), BBC (Bromebenzyl cyanide) CN-DM (Burning mixture of CN DM) CNS (Chloracetophenone & chlorpicrin), DA (diphonyl chloroarsine), DM (Adamsite, diphenslamino chloroarsine)
Chemical Warfare Agents	GB, VX Lewisite, Sulfur mustard (H, HD) Nitrogen mustards
Pyrotechnics and Incendiaries	Napalm, Thickened gasoline w/napalm, PTI (incendiary mixture), SGF_2 smoke mixture

product. For food manufacturing (SIC Code 20), meat products (SIC 201), canned foods (SIC 203), and beverages (SIC 208), the waste factors were 1.42, 0.89, 4.2, and 0.2 pounds per dollar, respectively. Since these factors are based on the value of the 1972 dollar, appropriate adjustments have to be made to compensate for the effect of inflation. It is not clear, however, what fraction of the above waste generation factors represents wastewater treatment sludge.

Primary treatment of meat packing wastes was reported to yield about 8 tons of sludge per million gallons of waste processed at one plant.[14] This large sludge yield was due primarily to the high solids content of the raw waste. Secondary treatment of the waste by trickling filter produced about 1.6 tons of sludge per million gallons.

Generally for biodegradable industrial wastes, the quantity of sludge generated in secondary treatment depends on the degree of stabilization or oxidation achieved. For example, dairy wastes when completely oxidized are known to produce little or no sludge requiring disposal.

The nature and mode of disposal of sludges containing non-hazardous organics, derived from meat packing plants, canning plants and grain mills are presented in Table 23. Treatment and disposal similar to those cited in this table can also be used for the sludges from dairy, fermentation, sugar, and starch industries.

Waste Residuals from Other Industrial Categories

In addition to those already discussed the following industrial waste categories are known to discharge hazardous organic compounds: (1) industrial inorganic chemicals, (2) metals mining, (3) pharmaceuticals, (4) petroleum rerefining, (5) leather tanning, (6) metal smelting and refining, (7) electroplating and metal finishing, (8) special machinery manufacturing, (9) electronic components manufacturing, and (10) storage and primary batteries.[15] Table 17 summarizes the quantities of hazardous waste generated in some of these categories which generate residuals that are primarily organic in nature and the disposal technology in use. Industries such as battery manufacture, leather tanning and finishing, meal smelting and refining, etc., produce potentially hazardous wastes. The degree of their hazard is primarily due to the heavy metals contained in them. Leather tanning and electronic component industries generally depend on treatment technology conventionally used for municipal wastewater to process their wastewaters. The primary and secondary sludges produced in these industries are considered potentially hazardous because of their heavy metal and fluoride content.

As the level of treatment is raised and as pretreatment of wastewater is provided in some of these industrial categories, the production of biological sludge will increase. The ultimate waste disposal technology for most of these wastes is land disposal either on-site or off-site. Incineration is also used for the disposal of some industrial waste residual streams as is indicated in Table 17.

WASTES FROM SERVICE INDUSTRIES

The nature of waste residuals generated in a service industry depends of course on the type of service provided. The agricultural service industry for example provides services involving use of pesticides. The hazardous residuals are associated with unused waste pesticides, pesticide containers, and dilute pesticide solutions generated from rinsing operations.[16]

Pesticide Application Industry

In a study dealing with the disposal of waste pesticides, it was reported that on an average, 93 ml of residue was left unused per container with a range of 45-221 ml/can.[16]

The common methods for disposal of dilute pesticide solutions resulting from rinsing cans and applicator tanks include discharge to ground surface with subsequent uncontrolled runoff, collection and application to small land areas near the mixing site, contractor removal of residues settled in a pond, discharge to a pond with subsequent seepage into the ground, and crop application.

With the promulgation of RCRA regulations, disposal practices will be upgraded. Triple-rinsed containers will have to be disposed of in a licensed landfill, an approved practice. Controlled incineration will be needed for unwanted pesticides. Dilute solutions of pesticides may be applied to crop land, but this may not always be feasible. An alternative technology employing a system of mounds involves collecting the pesticide waste solution in a lined earth impoundment and permitting it to evaporate and degrade. The concentrated pesticide with its associated soil can then be disposed of.

The cost of disposing unrinsed containers in a secured landfill was estimated to be $55/metric ton according to an EPA funded study. Incineration costs of unwanted pesticides was estimated to be $80/metric ton. The operating costs of a high quality soil mound system for the disposal of 450 gal/day of dilute pesticide rinse water at an average of 225 days/yr was estimated to be 0.095¢/gal. The approximate total capital cost for this soil system was estimated at $12,850.[17]

Table 17. Type and Quantity of Hazardous Waste Residuals and Waste Disposal Practices in Industrial Inorganic Chemical, Pharmaceutical, and Petroleum Rerefining Industries

Industrial Category	Type of Hazardous Waste Residuals	Quantity yr. 1977	Hazardous Waste Quantity Produced as Percent of Total	Disposal Methods
Industrial Inorganic Chemical, SIC 281	Chlorinated hydrocarbons	1,200 (wet tons)	~0.06	Secured landfill incineration
Pharmaceuticals	Mixed solvents	15,400 (")	~21	Incineration
	Non-Halogenated solvents	26,900 (")	~37	Incineration
	Halogenated solvents	3,900 (")	5	Incineration
	Organic chemical residue	15,000 (")	~21	Incineration 79.5% Landfill 12.5% Sent to biological wastewater treatment plant, ~8%
	Aqueous mixed solvents	2,800 (")	~4	Biological wastewater treatment ~4.6%, incineration 95.4%
	Aqueous alcohol	700 (")	<1	Incineration
	Antiviral vaccines toxoids serum	580 (")	<1	Crushed, diluted and sent to biological wastewater
	Returned good and contaminated or decomposed active ingredients	600 (")	~1	Treatment ~20% Landfill ~70% Incineration ~10%
Petroleum Rerefining	Oil in acid sludge	13,000 (dry tons)	17.5	Landfill
	Oil in caustic and other sludges	5,600 (")	7.5	Recycled or reused
	Oil in spent clay	4,000 (")	5.4	Landfill

Drum Reconditioning Industry

In the drum reconditioning industry, firms accept empty drums from various sources for restoration. This industry may also arrange for disposal of any residual oils and chemicals contained in the drums.

The waste streams from drum cleaning operations include: (1) pre-dump wastes, if any, (2) caustic sludge, and (3) incinerator sludge/ash. These wastes vary widely in their characteristics not only from plant to plant, but also from hour to hour. The caustic bath may contain in addition to several inorganic compounds, organic compounds such as toluene, xylene and naptha which are used as paint solvents.

Oil drums can be reconditioned with little difficulty. Waste oil is readily incinerated and pre-dump wastes are sold for reclaiming operations. Some plants discharge their wastes to sewers. A status of the current waste disposal practices and those specified by RCRA has been reported in a summary form[16], and is presented in Table 18. The cost for off-site disposal of wastes originating from drum reconditioning plants has been reported to be $55/metric ton.[16]

Gasoline Service Stations and Related Industry

It has been estimated that about 171,000 gasoline service stations, auto repair shops and other related industries were in operation in 1978.

The main waste streams from these commercial firms are waste oil from crank cases and hydraulic oil from automatic transmissions. In addition to containing high concentrations of lead, zinc, and barium, the waste oil is also reported to contain organic compounds such as PCBs, 2, 3, 7, 8-tetrachloro dibenzodiorin, 2, 4, 5-trichlorophenol, and polycyclic aromatic hydrocarbons.

The estimated quantity of waste crank case oil and hydraulic oil generated by the above categories of industries in 1978 is summarized in Table 19.

Waste oil from this industry is either stored on-site in underground tanks (capacity 500 gallons) or stored above ground in 55 gallon drums. It is generally collected by a waste oil collector who then disposes of it by using it for any of the following purposes: (1) fuel, (2) road oil (including dust control), (3) re-refining, (4) asphalt extender, and other construction uses, (5) weed control, and (6) input to miscellaneous manufacturing processes. It was reported that about 470 million liters of waste oil was re-refined in 1977.[16]

RESIDUAL MANAGEMENT TECHNOLOGY

The treatment of industrial waste residuals, such as the biological waste treatment sludges and non-aqueous sludge streams may be accomplished by various unit processes. They range from those applied usually in municipal sludge treatment (e.g., chemical conditioning, thickening, dewatering, sludge stabilization by aerobic and anaerobic digestion, etc.) to chemical fixation, detoxification, encapsulation, and incineration, which are applied selectively to some categories of industrial sludges. Process sludge streams if not hazardous may be transported by pipe, road or by barge for land reclamation. Also, they may be detoxified, chemically fixed, or incinerated and the residue may be disposed of on land in a safe manner. Some of the important unit operations are briefly described below.

Sludge Conditioning

The conditioning of biological waste treatment sludges and some industrial sludges such as petroleum refinery sludges is usually accomplished by addition of chemicals such as ferric chloride, lime, and a combination of ferric chloride and lime. Organic polymers have also been used with success. The dosing rate for these

Table 18. Summary of Wastes and Disposal Practices in Drum Reconditioning[16]

Waste Stream	Current Disposal	RCRA Specified Disposal
Pre-dump	Landfilled or incinerated	Secure landfill or controlled incineration
Caustic Sludge	To municipal sewer, municipal or private landfill	Secure landfill
Incinerator ash/sludge	Municipal or private landfill	Secure landfill

Table 19. Annual Waste Oil Quantities Produced in the Automotive Service Industry

Type	Total Waste Oil (Million Liters)
Gasoline Service Stations	695.9
Automobile Repair Shops	206.1
New Car and Truck Dealers	272.2
Automobile Fleets	88.7
Total	1,262.9

conditioning agents varies quite widely depending on the nature of the sludge, the dewatering process and the chemical used. Since several conditioning agents are available on the market, it is advantageous to test and screen a number of them in the laboratory in choosing one for a given sludge stream. Criteria for the selection of a conditioning agent are usually based on (1) solids captured upon dewatering a sludge after its conditioning, (2) clarity and amount of supernatant, (3) floc strength of the dewatered sludges, and (4) the dosage rate and the cost of the conditioning agent.

There are several unusual methods described in the literature for conditioning residuals separated from wastewaters. These include (1) alternate freezing and thawing, (2) heat treatment, (3) solvent extraction, (4) electrical treatment, (5) ultrasonic treatment, and (6) bacterial treatment. Application of these techniques is not extensive, however.

Phase separation by the use of solvent extraction has been reported for petroleum refining sludges.[18] Sludges derived from industries such as pulp and paper manufacture, steel production, wool scouring, slaughter house operations, (paunch manure and blood), wastes from shrimp packing, and some mixed industrial sludges are also amenable to such a treatment.[19]

Sludge Concentration

Sludges are concentrated prior to their stabilization. One such process is thickening in which liquid is removed to increase the solids concentration of the sludge to about 10%. The degree of thickening depends on the amount of water removed. Thickening accomplishes the following: (1) reduce the sludge volume to be handled, (2) reduce the cost of chemical conditioning, a process which is generally practiced prior to sludge dewatering, (3) improve digester operation and reduce the cost of digester operation because of less space required due to increased solids loading per unit digester capacity and less supernatant production, (4) reduce the amount of water to be handled prior to digestion and dewatering operations and thus produce a lower volume of sludge to be handled, and (5) equalize to a significant extent the quality and quantity of sludge.

Thickening is accomplished by (1) gravity, (2) dissolved air flotation, and (3) chemical conditioning. These unit processes are used in several industries as in the case of a municipal treatment plant to increase the solids concentration of dilute sludge suspensions.

Another process is dewatering in which water is removed from a sludge suspension so as to concentrate it to a suspended solids concentration of greater than 10%, preferably to over 15%. Dewatering usually connects sludge into a non-fluid form and renders it amenable to ultimate disposal by landfilling, heat drying followed by utilization and/or disposal, lagooning, composting followed by land application, and incineration.

There are several ways to accomplish dewatering. These include unit processes such as: (1) vacuum filtration, (2) centrifugation, (3) filter pressing, (4) screening, and (5) sand bed dewatering. In filtration processes such as vacuum filtration, screening and sand bed dewatering, a dilute suspension of solids moves through a porous medium such that suspended particles are retained by the porous medium and a relatively clear liquid is produced. The centrifugation process involves the separation of solids from the liquid by means of sedimentation under a centrifugal force. This process is generally competitive technically and economically with other dewatering devices such as vacuum filters and filter presses, and is more capable of dewatering sticky and gelatinous sludges.

In comparison to other processes, filter presses yield a sludge cake with the highest percentage of solids. These units are being used increasingly for dewatering wastewater treatment sludges.

Table 20 summarizes common thickening and dewatering equipment with typical operating conditions and applications to the processing of sludges.[20]

Industrial sludges which are biodegradable may be processed initially by chemical conditioning and thickening, and then stabilized by processes such as aerobic digestion, anaerobic digestion, composting, etc. The aerobically or anaerobically digested sludges still have a very high water content and need to be dewatered for ultimate disposal. Techniques such as sand bed dewatering, centrifugation, vacuum filtration, or storage in lagoons may be employed to obtain a product with a high solids content. The centrifuged and vacuum filtered sludges may be heat-dried, or composted, to obtain a product with a relatively low moisture content which can be disposed or utilized on land, or, it may be incinerated. The ash produced in this operation is disposed of on land in a safe manner.

Incineration

Incineration may be applied for the treatment and disposal of sludges and involves drying and combustion of waste residuals. It has been applied to many types of sludges from industries such as organic chemicals, pesticides, explosives, paint, rubber, plastics, textiles, petroleum refineries, etc.

The factors that govern the process include the fuel value of the residuals, rate of air supply, time for combustion, temperature of the incinerator, and turbulence. Any water contained in the sludges needs to be evaporated before combustion of the waste residuals can be initiated. Heat is generated in the incineration process. The difference between the heat generated and the heat lost via radiation, stack gases, and ash, is conserved and used for heating the sludges and the process air. Additional heat required to burn the sludge is supplied by supplemental fuel. The end products of incineration are usually CO_2, water vapor, SO_2, and inert ash. Traces of other stack emissions such as halogens and oxides of nitrogen are also usually detected.

Table 20. Sludges Thickening and Dewatering Equipment[20]

Equipment Type	Feed Rate (gpm)	Solids Concentration %	Solids Capture (% solids)	Output Cake Conc. Range (% solids)	Applications	
					Primary	Secondary
Stirred Gravity	10-3,000	—	95-98	5-10	Primary and secondary, metallic, chemical	Industrial
Air Flotation	10-10,000	—	92-98	5-10	Waste-activated, lime, flocculated alum	Primary, secondary, industrial trickling filter
Centrifuges						
Disc	25-300	0.2-1	90-95	5-10	Waste-activated	
Scroll	5-300	0.5-15	60-95	20-45	Raw or digested primary or secondary, alum, lime	Industrial
Basket	10-60	1-10	90-95	5-25	Waste-activated, lime, alum	Hydroxide
Filters						
Vacuum Drum	0-250	8-10	50-99	20-40	Digested primary or secondary	Chemically precipitated
Vacuum Belt	1-50	5-10	75-90	15-25	Industrial	Clarifier overflows
Pressure	10-250	2-5	95-99	20-50	Alum, waste-activated, hydroxide	Municipal, industrial chemical
Belt	5-200	4-6	95-99	20-35	Secondary biological	Petrochemical, industrial
Dual Cell Gravity	10-500	0.5-5	90-98	10-20	Primary and secondary	Metal hydroxide

Incineration of waste residuals may be conducted on a batch or a continuous basis depending on the amount of material to be incinerated.[21] Various types of incinerators are available for the disposal of industrial residuals containing hazardous organics including the popular multiple hearth and the promising fluidized bed incinerator.[22,23] The advantages and disadvantages of a number of incinerator types are presented in Table 21.

A detailed study of the applicability of thermal destruction processes such as incineration, pyrolysis, and wet air oxidation, was performed jointly by the TRW Defense and Space Systems Group and by the staff of the Arthur D. Little Company for the USEPA. This study focused on the treatment of various organic industrial wastes, including an API separator sludge, a phenolic sludge, and a polyvinyl chloride waste sludge.[21] These wastes were treated by pyrolysis, fluidized bed incineration, and rotary-kiln incineration, respectively. The characteristics of these wastes, operating conditions of the unit processes, and results of performance are given in Table 22.

The API waste sludge was processed through a pyrolysis-incineration system consisting of a rotary-hearth pyrolyzer coupled to a rich fume incinerator for the combustion of the pyrolyzer effluent gases. The results of this study indicated that a 70% conversion efficiency of the waste to a more useful form was realized for utilization in the incineration system. In light of the test results, the TRW and A.D. Little Company study recommended that pyrolysis should only be considered in conjunction with a heat recovery system particularly with wastes having a high BTU value. The estimated capital and operating costs for processing 22,800 metric tons per year was estimated respectively at $6.07 million or $140/metric ton (mt) of which the auxiliary fuel costs were $37.50/mt.

The incineration of phenolic waste sludges produced from the scrubbing operation of gasoline with alkali to remove H_2S and phenol was found to be feasible. The results of this investigation, indicated that a high efficiency of waste destruction (>99.9%) was achieved (Table 22). Constituents originally present in the wastes could not be detected in the combustion gases, scrubber water, or sand used in the incinerator.

A rotary kiln incinerator was used to process a PVC waste sludge which had high solids content. This sludge is potentially hazardous because of the vinyl chloride monomer contained in it. The operating conditions of the tests are given in Table 22. The results of these tests indicated that very high efficiencies were achieved in destruction of waste and organics. No vinyl chloride monomer was found in the combustion gases. The capital and operating costs for processing 6,700 metric tons of PVC waste/year were estimated at $7.8 million or $582/mt.

The successful development and implementation of a fluidized bed incineration system by the Battelle Laboratories for the disposal of wastes resulting from wood pulp production led them to study its applicability for the disposal of waste residuals from paint, plastics, rubber and textile industries.[22]

Based on a detailed investigation of the conditions of operation of the pilot scale incinerator, including analysis of data on influent wastes, effluent gases and scrubber water, the study made the following conclusions:

(1) Fluidized bed incineration was technically feasible for all the wastes studied. In incinerating solvent recovery sludges from the paint industry, supplemental fuel was not necessary because of their high heat content. No noxious materials were found in the exhaust gases, gas scrubber effluent, and residue. An operating cost of 1.1¢/lb waste (1972 basis) was estimated for an incinerator serving a typical plant.

(2) Incineration of PVC and styrene wastes resulted in no noxious or toxic materials, with the exception of HCl in the gas scrubber effluent. Although these wastes are currently disposed of in landfills, incineration may provide an economic alternative.

(3) No noxious or toxic compounds were generated in the incineration of the rubber waste. The operating cost was estimated at 0.4¢/lb in an installation sized for a typical plant.

Table 21. Advantages and Disadvantages of Various Types of Incinerators[10]

Type	Uses and Advantages	Disadvantages and Limitations
Solid Stationary Hearth	1. Low capital 2. Potential of tight air control with an airlock feeder. 3. Used for incineration of solids. 4. Can be designed to include liquid incineration.	1. No turbulence, mixing or aeration. 2. Slow burning rates. 3. Batch operation. 4. Manual ash removal. 5. Does not lend itself to good air pollution control.
Solid Hearth (Rotary Hearth or Rabble Arms)	1. Continuous ash discharge. 2. Capable of incinerating waste solids independently or liquids and solids in combination. 3. Widest practical turn down ratio. (Maximum to minimum operating range). 4. Incinerating materials will not fall through hearth. 5. Adaptable for use with a gas scrubbing system.	1. Rabble arms or plows are susceptible to damage. 2. Limited turbulence and air contact. 3. Partly combusted materials may flow out ash discharge. 4. Solid wastes fed at intervals. An air lock system should be used to improve combustion characteristics and control. 5. Arched, self-supported multiple hearths made of refractory material are vulnerable to abrupt temperature variations with resultant downtime and cost increase.
Rotary Kiln	1. Will incinerate a wide variety of liquid and solid wastes. 2. Capable of receiving liquids and solids independently or in combination. 3. Not hampered by materials passing through a melt phase. 4. Feed capability for drums and bulk containers. 5. Wide flexibility in feed mechanism design. 6. Provides high turbulence and air exposure of solid wastes. 7. Long inventory time for slow burning refuse. 8. Continuous ash discharge. 9. No moving parts within the kiln. 10. Adaptable for use with a wet gas scrubbing system.	1. High capital cost installation for low feed rates. 2. Cannot utilize suspended brick in kiln. 3. Operating care necessary to prevent refractory damage. 4. Airborne particles may be carried out of kiln before complete combustion. 5. Spherical or cylindrical items may roll through kiln before complete combustion. 6. Kiln incinerators frequently require excess air intake to operate due to air leakage into the kiln via the kiln end seals and feed chute, which lowers fuel efficiency. 7. Drying or ignition grates, if used prior to rotary kiln, can cause problems with plastics melt plugging grates and grate mechanisms.

Fluid Bed	1. Capable of incinerating a moderate range of liquid and solid wastes. 2. Rapid heat transfer from gas to solid. 3. High combustion rate. High turbulence and air exposure. 4. Low excess air requirements. 5. Large heat sink to smooth out fluctuations in feed rate or fuel value.	1. Requires fluid bed preparation and maintenance. 2. Feed selection must avoid bed damage. 3. May require special operating procedures to avoid bed damage. 4. Incineration temperatures limited to a maximum of about 815°C (1500°F).
Stationary Liquid Waste Burner	1. Capable of incinerating a wide range of liquid wastes. 2. May use suspended brick. 3. No continuous ash removal system required other than air pollution controls.	1. Must be able to atomize tars or liquids through a burner nozzle except for certain limited applications. 2. Heat content of liquids must maintain adequate temperatures or a supplemental fuel must be provided. 3. Must provide for complete combustion and prevent flame impingement on refractory.

(4) Incineration did not appear promising for viscose rayon waste because of the presence of low melting point inorganic waste materials. Other wastes generated in textile mills are too dilute and may not be amenable to incineration.

Wastes from the manufacture of explosives are also amenable to incineration. This was the conclusion reached by the Manufacturing Technology Directorate Picatinny Arsenal, Dover, New Jersey who evaluated six incinerator designs and concluded that the fluidized bed incinerator was superior to others.[12]

Evaporation

Evaporation may be used for concentrating waste residuals. This process may be particularly attractive in areas where adequate solar radiation is present and rainfall is low.

Evaporation ponds are appropriate where land is inexpensive and climatological conditions permit rapid rates of evaporation. The size of the evaporation basins is dependent on the amount of waste to be processed and the rate of evaporation. Concrete tanks, large earthen tanks constructed in reasonably impervious areas, or ponds constructed with impervious lining materials to prevent seepage are generally used as evaporation basins. Where large ponds are used appropriate measures should be taken to divert runoff, protect wildlife, and prevent odor problems.

In order to enhance the rate of evaporation, surface aerators may be provided. In addition to evaporation, other solids concentration processes may occur in ponds including sedimentation of particulates and precipitation. Chemical and biochemical degradation of some compounds may also proceed. Sludge deposited in these ponds over a period of time should be dredged periodically and disposed of in a secured landfill. Evaporation also takes place in lagoons where sludges are stored thereby increasing their solids content.

Table 22. Destruction of Industrial Sludges by Thermal Processes

Wastes & Characteristics	Unit Process & Operating Conditions	Performance
API Separator Bottoms	Pyrolysis/Incineration	
a. Water 70% b. Organic Materials 13% (≃42.7%, aliphatics rest aromatics)	a. Feed rate: 4.7 to 25.3 kg/hr. b. inert gas flow 42.5 m³/hr.	70% of feed organic conversion to a useful form Ash=20% of total feed
c. Ash ~ 10%	c. Temp. 760°C.	85% of the ash is inorganic
d. BTU: 2500/lb	d. Residence Time: 12.5 min.	Particulate Stack emission 23-88 mg/m³
	e. Temp. Incinerator 830:C.	
Phenol Waste Sludge	Fluidized Bed Incineration	
a. Water: 86%	a. Feed Rate: 34-50 1/min.	a. Destruction Efficiency
b. Solids: 14%	b. Residence Time: 12-14 secs.	i. Total organics: 99.93 - 99.95%
c. Ash: 5.5%	c. Bed Temp: 740-757°C.	ii. Waste Constituents >99.999%
d. <1% Phenol & Cresols	d. Free Board Temp. 813-899°C.	b. Particulate stack emission 1280-1430 mg/m³
e. BTU: < 1050/lb.	e. Waste/Auxiliary fuel, 1/1 2.3-3.0	c. Total organics in scrubber water-Not detected
PVC Waste Sludge	Rotary Kiln Incineration	
a. Water: 72% b. Solids: 28%	a. Feed Rate: 0.845 mt/hr. b. Residence Time: 3 secs.	a. Destruction efficiency i. Total organics: >99.995% ii. Total Waste: 99.8-99.88%
c. Ash ≃ 2%	c. Primary combustion zone temperature 870°C.	b. Particulate stack emission 70.9-71.4 m³
d. VC monomer ≃ 200ppm	d. Secondary combustion zone temperature: 980-1090°C.	c. Total organics in scrubber water: 0-5.6 mg/L
e. BTU: 400/lb.		

Certain waterborne wastes like those from organic chemicals and pesticide industries are too dilute to be effectively disposed of on land or by incineration. A review of pollution control technology in the pesticide formulation industry indicated that solar evaporation of the wastes is practiced extensively. Evaporation ponds without any discharge are also identified as the best practicable technology for the disposal of these wastes.[10]

Other liquid wastes that are amenable to evaporation as a disposal method are wastes from the inorganic chemicals and explosives industries, and certain types of radioactive wastes. Wastewater from scrubbers associated with an incinerator may be concentrated by evaporation, and the residue disposed of on land.

Multiple effect evaporative techniques similar to those used for distillation of seawater have been applied for dewatering sewage sludges. This technique, known as the Carver-Greenfield process,[24] facilitates the evaporation of water contained in the sludge by using oil as a fluidizing medium. Following evaporation, the oil is separated from the sludge by a centrifuge and is recycled to the incoming sludge. A very dry product is obtained in this process. This process has been applied with some modifications to process residuals from pharmaceutical and pet food industries.[25] With these wastes, after dry solids are obtained by the evaporative technique, a pyrolized unit decomposed the organic residue to hydrocarbons which were then used as a supplemental fuel to the boiler burner. The ash obtained in this process can either be used in road paving asphalt or disposed of on land.

Other Methods

Various other methods may be used for the processing of residuals. An Arthur D. Little study conducted for the EPA surveyed 47 different processes for the treatment of solid, semi-solid and liquid industrial wastes.[26] It identified a number of methods for the treatment of organics contained in industrial residuals including distillation, calcination, and hydrolysis. (These are usually employed in special cases for the stabilization and disposal of industrial waste sludges.)

Distillation may be used for the recovery of organic solvents and is basically used in solvent recovery plants. It may also be used for processing wastes from paint industry, and lube oil recovery. However, this method is not suitable for thick slurries and sludges.

Calcination is a process that may be operated at atmospheric pressure in which theoretically no interaction between material being processed and a gaseous phase (e.g., air as in incineration) takes place. At high temperatures, usually 650-1100°C, vaporization of water takes place, organics are destroyed and a solid mass results due to the fusion of the inorganic material. Additives like silicates and phosphates may be used to decrease the leachability of the solid residue. This process may be utilized as a one-step process for treating complex wastes to concentrate, destroy and detoxify organic residues. A disadvantage of this process is that the costs will be very high, if the wastes have a large amount of water. About 20×10^6 BTU/ton of dry solids would be required for the calcination of a sludge having 90% moisture. Hence, supplemental fuel will be needed. The greater the organic content and the lower the moisture content of a sludge, the lower is its fuel requirement. Gaseous and particulate emissions produced in this process cannot usually be discharged to the ambient air. Therefore, air pollution control equipment is generally required.

Different types of calciners are available including (1) open hearth, (2) rotary kiln, and (3) fluidized bed units. The choice of equipment depends largely on the type of waste to be handled. For example, the fluidized bed calciner can be used for liquids, slurries, sludges and solids, whereas the multiple hearth or rotary kiln types are better suited for solids and sludges. A fluid bed calciner at an oil refinery in India has been reported to process a mixture of sludges from various units viz, dissolved air flotation unit, API separator, tank cleaning, wastewater treatment, etc.

Although not widely used for processing industrial sludges, hydrolysis reactions may be carried on with suitable feed streams such as waste slurries and sludges at elevated temperatures usually with the addition of acids, alkalies, or enzymes. In the petroleum refinery industry, the sludge from acid treatment of light oils may be hydrolyzed to recover sulfuric acid. A tarry product containing some organics formed in this process may be disposed of by incineration. Hydrolysis has also been shown to be a useful technique for production of sugar from refuse, and the conversion of organic sludge to animal feed.

The above methods can be applied to different hazardous and non-hazardous industrial waste sludges. The appropriateness of a given method for a given sludge depends on its characteristics, amenability to a specific technology, and economics. Table 23 shows the technology that may be considered for the treatment of some non-hazardous and hazardous industrial sludges. The term "land-based technology" used in this table encompasses any ultimate disposal technique by which sludge is applied to land either for land reclamation, growing crops, or for the sole purpose of using land as the final locus for sludge deposition.

Disposal - Current Practices

Land based technology and incineration (controlled and uncontrolled) are the methods most widely employed for the ultimate disposal of industrial waste residuals.

Industrial waste residuals may be disposed of either on-site where they are generated or off-site. On-site and off-site treatment/disposal methods include storage, material recovery, landfilling/dumping, lagooning, landspreading, and incineration.

Landfilling operations may range from indiscriminate dumping to a controlled management of disposal of wastes in secured landfills, that is landfills which ensure adequate environmental and health protection. Landspreading involves the transportation of a sludge to a site where it is applied. The sludge is usually hauled by a truck and is applied uniformly on the land. The actual application rate is usually determined by experience and varies from sludge to sludge. It depends on the nature of the waste, the assimilation capacity of the soil, climatological conditions, and the amount of land available. The sludge moisture is allowed to evaporate and then the residuals are rototilled into the land. Where the soil has the ability to detoxify or render innocuous the hazardous organic compounds contained in the sludge, landspreading of sludge may be considered as a treatment and disposal technique.

Disposal of sludges in lagoons, ponds, sumps, and open pits is also a mode of ultimate disposal but one that is not as environmentally satisfactory as disposal in secured landfills. Indiscriminate disposal of sludges in lagoons, open pits and ponds may pose environmental and health hazards. However, when lagoons are properly constructed and operated, the environmental damage is reduced. Their environmental acceptability depends primarily on the method of construction, materials used in construction, site-specific considerations such as hydrogeologic properties of the land involved, and the type of waste disposed.

Irrespective of whether the residuals are disposed on-site or off-site by a given method, an important technological consideration is to ensure that the land receiving the wastes is suited for application of the hazardous wastes without causing any environmental degradation. Considerations such as availability of land, machinery to apply the sludges, man power, availability of an incinerator and other site-specific factors dictate whether the sludge may be disposed of on-site or should be disposed off-site. Where land is available and incineration is not required to dispose of the sludge, obviously the choice would be of an on-site land-based technology. Even though land is available, if incineration is necessary to dispose of an industrial sludge and one is not available on-site, the sludge has to be hauled to an off-site facility. Data on the quantity of waste residuals disposed by various industries either on-site or off-site are summarized in Table 24.

Table 23. Residuals Generated from Non-Hazardous and Hazardous Industrial Wastes and Their Treatment and Disposal

Industrial Category	Type of Sludge or Semi-Solid Waste	General Treatment	Disposal Methods
Non-Hazardous Wastes			
Meat Packing	Waste Treatment	Anaerobic and Digestion Lagooning	Land-based Technology (Irrigation)
Canning	Fruit and Vegetable Waste	By product recovery (alcohol and ensilage production) Incineration	Animal Feed Land-based technology
	Sludge produced in municipal treatment plants by discharging canning wastes	Municipal treatment technology	
	Liquid organic residuals		Spray irrigation
Grain Mills	Steep water	By product recovery	Land-based technology
	Fiber Solids	Lagooning	
	Sludge produced in municipal treatment plants by discharging grain mill wastes.	Municipal treatment	Land-based technology
Hazardous Wastes			
Paper & Allied Products	Sludges	Conditioning, Dewatering Landfarming	Land-based technology Incineration
Paint Formulation	Latex Paint Wastes	Physico-chemical procedures, Sedimentation, Municipal Treatment Technology applied to sludges from latex paint wastes	Land-based technology

Leather Tanning	Semi-solid Wastes Containing hair, fleshing, trimmings, dirt, and manure	Screening and Sedimentation	Land-based technology
	Sludge produced in municipal treatment plants due to discharge of leather tanning wastes	Municipal Treatment Technology Incineration	Land-based technology
Petroleum Refinery	Different types of aqueous and non-aqueous sludges	Conditioning thickening and Digestion Land Farming Stabilization, Solidification	Land-based technology Incineration
Medical and Other Health Services	Not sludge, but semi-solid and solid wastes comprised of isotopes, bacteriological specimens, drugs, disposable medical supplies, general rubbish		Encapsulation of isotopes, autoclaving of pathological specimens, and ultimate disposal by land-based technology
Organic Chemicals	Process waste streams, and off-grade products	Dilution of some streams and disposal to sewage treatment plant	Land-based technology Deepwell disposal of liquid wastes, incineration
Pesticides and pesticides formulation	Various process streams containers with residual pesticides	Containment in lagoons and evaporation	Incineration, storage in sealed drums and burial in land in a secure manner
Explosive	Red water, explosive contaminated inert wastes	Evaporation of red water and incineration of concentrates. Red water acidification and steam stripping	Secure landfill, controlled incineration
	Waste explosives	Incineration Composting of waste explosives	Spray irrigation
	Explosive contaminated inert wastes	Incineration	Incineration

Table 24. Quantities of Residuals Disposed of by Different Methods in On-Site and Off-Site Facilities by Various Industries (Wet Tons/yr, 1977 basis)

Industrial Category	Waste	Method of Disposal	On-site	Off-site	Unknown or Other
Plastic & Synthetics	Liquid Phenolics	Drum storage	161,000	—	—
	Phenolic sludges	Drummed or Lagooned	44,000	—	—
	Amino resins	Incineration	—	20,700	—
	Still bottoms	Incineration	27,100	27,100	—
	Wastewater Sludges	Mostly unknown	—	—	284,000 (some land disposal)
Pharmaceuticals	Organic chemical residue	Incineration	6,120	5,800	1,530 (disposal to biological) treatment plant after dilution)
		Landfill	—	1,800	
	Mixed solvents	Incineration	6,240	9,160	
	Non Halogenated solvents	Incineration	10,740	16,200	
	Halogenated solvents	Incineration	870	3,000	
	Aqueous Mixed solvents	Incineration	970	1,700	90 (disposal to Biological Waste Treatment Plants)
	Aqueous alcohol	Incineration	280	400	
	Antiviral vaccines	Incineration	115	120	115 (autoclaved on-site and ash disposed off-site)
	Other Biologicals	—	—	—	270 (autoclaved on-site and ash disposed off-site)
	Returned goods and contaminated or decomposed materials	Incineration	60	—	120 (slurried with water and disposed in biological wastewater treatment plant)
Paints & Coatings	Wastewater sludge	Incineration	5	50	
		Landfill	70	1,470	

	Waste organic cleaning solvent	Incineration	5	20	
		Landfill	50	950	
	Spills and spoiled batches	Landfill	70	1,470	
Organic Chemicals	Organic chemical waste	Landfill	483,000	113,000	
		Incineration	~2,250,000	51,000	
		Biological Treatment/ Lagoon	565,000	—	
		Deepwell	6,540,000		
Pesticides	All types of pesticide wastes	Landfill	175,000	75,000	
		Incineration	—	100,000 (>95% in off-site)	
		Storage in drums or piles	81,000		
		Unspecified	—	—	144,000 (usually detoxified and disposed either on-site or off-site)
Explosives Private industry	Fixed High Explosive waste	Open Burning	> 387	—	
		Chemical detoxification followed by land disposal	—	—	26
Government owned and contractor operated explosives	Explosive wastes	Open Burning	4,800		
	Explosive contaminated inert wastes	Open Burning	13,700		
		Landfill	1,000		
	Other (red water, RDX/HMX waste)	Open Burning	90		

	(water, organic solvents, etc.)	Landfill	140	
Petroleum Refining	All wastes	Landfill	355,000	535,000
		Lagoon	284,000	289,000
		Landspreading	334,000	—
		Incineration	40,000	4,000
Rubber Products	Oily Wastes	Landfill	—	1,000
	Air pollution equipment dust	Landspreading	70	—
		Landfill/dump	1,950	39,200
Leather Tanning and Finishing	Trimmings, shavings, finished and unfinished leather trim, wastewater screenings residues from buffing and finishing, wastewater treatment sludge	Landfill	4,800	97,000
		Dumps	1,900	40,600
	"	Certified facility	—	9,700
	Other sludges	Lagoons pits, ponds, etc.	5,300	13,500
Electronic Components	Waste Halogenated solvents & still bottoms	Landfill	200	2,200
	Waste Nonhalogenated solvents & still bottoms	Landfill	1,000	14,900
	Wastewater Treatment Sludges	Landfill	7,600	43,200
	Lubricating and Hydraulic Oils	Landfill	—	2,400
	Paint Wastes	Landfill	—	210
		Incineration	6	6

Arthur D. Little Company reported that on a national level the principal methods of hazardous waste disposal are landfilling and lagooning and stated that they will continue to be the principal methods of disposal in the future (Table 25).[27] This study also described the on- and off-site disposal practices in the various industrial categories. The extent of on-site disposal practices in these industries is given in Table 26. As can be seen from this table, on-site disposal of industrial residuals is quite prevalent in many industries. However, this mode of disposal has limited opportunities in densely populated areas.

Another national survey directed to the impoundments of wastes in the industrial sector, reported that there were about 110,000 industrial waste lagoons in the USA.[1] About 78% of impoundments served wastes from oil and gas, food products, textiles, chemicals, refining and mining industries, with another 12% servicing coal mining and paper making industries.

An excellent survey reported by Allegheny County, Pa., with respect to its industrial waste management, described landfilling of all types of sludges, reclaiming of materials, and incineration of tank bottoms and other organics as the primary modes of disposal.[28]

A Massachusetts survey based on the permits issued for the disposal of industrial residuals, reported that 85% and 24% of the waste solvents and oils, respectively, produced by the industries were reclaimed, whereas the remainder were incinerated for the most part.[29] This survey also indicated that while almost all the aqueous waste liquids produced (99.1%) were discharged to the local municipal wastewater treatment plants, other solids and sludges generated by the industries were disposed of by landfilling (56%) and incineration (41%).

In an elaborate survey conducted in 1978 via questionnaires submitted to State agencies, it was revealed that there were 14,392 landfills in the USA.[1]

A report by the Illinois Institute of National Resources indicated that landspreading of sludges was practiced by 71 industrial plants. Most of the sludges were assumed to be originating from food processing and similar industries. These sludges are considered to be organic and are biodegradable in nature and are hence appropriate for land treatment and disposal. The report also stated that the practice of landspreading sludges in Illinois appeared to be consistent with that of a 1977 USEPA estimate, which cited that 41% of the vegetable processing plants and 37% of the fruit processing plants used landspreading of sludge.[1] From the foregoing, it may be stated that land disposal of industrial sludges is by far the major prevalent practice.

Leachate and Ash Disposal—

Two important considerations in the ultimate disposal of industrial organic sludges are the management of leachate produced in land disposal sites and the disposal of ash resulting from incinerator operations.

A leachate may be formed from the sludges applied on land disposal sites under conditions of excessive precipitation. The quantity and characteristics of the leachate depend on the nature of the waste, processing of the waste, ability of the waste to leach, water holding capacity of the soil, initial moisture content of the waste and soil, permeability of soil, density of the waste, and the time over which the decay of the waste has occurred either in storage prior to disposal or in the soil itself. Depending on the hydrogeologic characteristics of the disposal field, the leachate may contaminate the groundwater table. In order to minimize the risk of groundwater contamination, the leachate should be managed properly. This can be achieved by installation of impervious liners in a land disposal site to intercept the movement of the leachate, and by collection and treatment of leachate.

Liners should be compatible with the waste disposed. Asphalt liners for example are not desirable when sludges containing solvents are disposed of because they react. The results of an EPA study, in which the compatibility of various liners with different types of industrial wastewaters and sludges was investigated, are presented

Table 25. Present and Projected Hazardous Waste Management Methods

Method	Percent Disposal	
	Present (1977)	Projected
Landfill	61.6	-
Secure landfill	-	68.2
Lagooning	29.7	21.5
Incineration	5.2	8.2
Landspreading	0.9	1.3
Deep well injection	3.0	3.0
Ocean	<0.1	-

Table 26. On-Site Disposal of Hazardous Wastes in Various Industries

Industry	% of Waste Managed On-Site
Electronic Components	13
Leather Tanning and Finishing	10
Petroleum Refining	44
Textiles	49
Pesticides	87
Plastics	80

in a recently published book on impoundments of industrial and hazardous wastes.[20] A list of various liner materials is also given in this book along with their properties. Polymeric membranes which are made of rubber and plastic membranes are gaining more acceptance because of their low permeability to water and other fluids. The procedure for the installation of a membrane liner is illustrated in a recently published report.[30]

Other lining materials for ponds include concrete, clay, and asphalt. Preliminary evaluations reveal the following ranking for durability of lining materials: (1) concrete, (2) plastic, (3) rubber, and (4) asphalt.[20] However, lined facilities are generally considered to be unacceptable in Illinois as a substitute for hydrogeologically safe landfills.[31]

The leachate formed is permitted to flow by gravity into collection sumps from which it can be removed and treated. The leachate may be processed by recycling, chemical fixation, encapsulation, evaporation, biological treatment, and advanced wastewater treatment. Physical-chemical processes were reported to be ineffective in removing the organics from leachate and biological pretreatment for biodegradable organics was required. Leachate from solid waste disposal sites may be treated in a municipal activated sludge treatment plant. However, a high strength leachate from such facilities could not be processed effectively in a test unit at a flow rate of >4% of the sewage flow rate.[32] Thus, the composition of leachate and availability of public treatment facilities are important considerations in selecting a leachate treatment method when the leachate is amenable to biological treatment.

It is important of course that all practicable steps be taken to minimize leachate production. In a study designed to evaluate methods to accomplish this objective the following alternatives were examined: (1) revegetation, (2) regrading to increase surface runoff, (3) surface sealing with an impermeable material, (4) construction of a slurry trench cut-off wall to prevent the movement of groundwater table, (5) installation of diversion ditches for the surface water away from the landfill, (6) lowering the groundwater table by developing a drainage system, and (7) counter-pumping to lower the groundwater table. In this study the first three methods were found to be most effective in minimizing leachate generation in a Connecticut landfill.[33]

Groundwater monitoring should be an integral part of any leachate management program. For soil and groundwater monitoring, samples from lysimeters and test wells located at different depths may be obtained and analyzed for their quality. Measurement of resistivity of soil core samples may also be employed to monitor the changes in ionic concentration of the soil samples. Baseline data on groundwater quality prior to the start-up of a new land disposal site should be collected so that deterioration resulting from landfill operations may be detected. Downstream monitoring of the groundwater quality is very important and if contamination takes place protective measures may be taken immediately.

The management of leachate involves long term planning and care, and should include the maintenance of records pertaining to waste inventories, analysis of monitoring data collected on a routine basis, continued analysis of groundwater even if the landfill site is closed, and clearly laid out contingency plans for removing the waste from the site, if needed, or to repair the landfill site or liners as and when required.

Disposal of ash produced by incineration of organic residuals comprises a facet of residual management. Ash is inorganic in nature and its content of various organic residuals depends on their nature. Some residuals like oily waste may contain as low as 1% of ash by weight whereas some sludges from papermills may contain as much as 50% or more. The ash content of different types of coal may range from 3 to 32%. High quantities of fly ash, and bottom ash or boiler slag are produced in coal burning electric power utilities. Particulate emissions scrubbed from incinerator stacks also resemble ash except that they are generally present as a sludge. The disposal of ash may constitute a serious problem if large quantities are encountered in incineration operations as in the case of service industries such as power generation facilities.

Ash is generally disposed of by wet ponding or dry landfilling. In wet disposal of the ash it is usually made into a slurry and pumped into a pond. After settling, the supernatant of the pond is returned to the plant and reused. Ponds are designed so that the wet ash slurry may be pumped to an elevated slope when the ash is separated from the liquid which is collected at the lower end of the pond. Ash can be dewatered by as much as 60-90% in well-designed and carefully operated ponds.

Landfilling of ash is usually carried out on-site in open dumps or by spreading. In order to avoid surface and groundwater contamination by the leachate, ash must be disposed of in a secured landfill or in a surface impoundment equipped with liners, leachate management protocols, monitoring wells, fencing, etc.

Ash may also be disposed by chemical stabilization, although this practice is not extensively practiced. This method has reportedly been used for flue gas desulfurization sludge, a wet-scrubbed particulate emission from power generation plants. The leachate of properly chemically stabilized ash should conform to RCRA regulations.

Evolving Technology

Organic compounds that are known to be toxic but which occur in low concentrations in industrial waste sludges may be treated by unit processes such as aerobic digestion, anaerobic digestion, composting, solidification, encapsulation, chemical detoxification, thermal destruction or by special landfill methods.

Aerobic and anaerobic digestion may be applied to sludges which are non-hazardous as is the case with sludges from food industries. This technology is fairly well established. Although composting is practiced for the stabilization of solid waste and municipal sludge, its application to the processing of industrial sludges is of recent origin. It has been reported that oils, greases, certain tars and wastes from the explosives industry have been composted with a certain degree of success, but application of composting for the stabilization of organics in different types of industrial sludges is not yet widely established.

Because of an inadequate technology for processing certain types of hazardous wastes and sludges, they are simply stored in containers. Examples of such wastes include various pesticides, hexachlorobenzene, PCB's and any number of unknown chemical wastes. In order to eliminate problems, such as leakage from containers, new processes have emerged including stabilization/solidification and encapsulation. This technology is of course not completely novel, as it has been in use for some time for the containment and disposal of radioactive waste. The methods employed are designed to produce a material that neither degrades nor produces a leachate.

Stabilization/solidification processes may be characterized as: (1) cement based, (2) lime based, (3) thermoplastic (using bitumen, paraffin, and polyethylene), (4) organic polymer, and (5) encapsulation.[34] Although these techniques are mostly applied to hazardous wastes containing primarily inorganics, it has been claimed that some proprietary processes have been used for sludges containing organics. A brief description of these techniques is given below.

In cement based solidification, the sludge is mixed with cement and other additives such as fly ash or incinerator ash to form a rock like material. Other proprietary materials are also used as additives. Materials such as clay and vermiculite are good adsorbents and can be incorporated into the cement. Sodium silicate has been found to be a good binding agent for contaminants in sludge, when it is added to the sludge-cement mixture.

There are several advantages to this technology. These are: (1) the process is amenable to variations in sludge characteristics and components, (2) the proportion of cement can be manipulated to control the strength and permeability of the product, and (3) the necessary equipment and materials to implement this technology are readily available. However, there are also some disadvantages: (1) the possibility exists that leaching of acid wastes will occur particularly from low-strength cement-waste mixtures, (2) the process is vulnerable to impurities in the waste which may affect the solidification process; hence, expensive pretreatment of the sludge may be required, (3) the bulk and weight of the finished product are increased.

The two most common additives in the method using lime for solidification are fly ash and cement kiln dust, which are also waste materials. Several proprietary additives are also available for solidifying the sludges. This method is similar to the cement-based in most respects and has similar advantages and disadvantages.

In the thermoplastic method, the waste is dried and mixed with materials such as bitumen, paraffin, and polyethylene at temperatures usually higher than 100°C. The mixture solidifies upon cooling. Often the mixture is placed in a steel drum or in a thermoplastic coating prior to disposal. Wastes containing solvents or chemicals that solubilize the additives or produce deterioration are not suitable for this process. The advantages of this process are: (1) leaching rates of pollutants are generally lower because the thermoplastic materials are resistant to most aqueous solutions, and (2) wastes adhere well to the thermoplastic materials. The disadvantages are: (1) waste must be in a dried form, (2) thermoplastic materials are flammable, (3) skilled labor and special equipment are required and hence, the process is expensive, (4) the method cannot be used for sludges containing solvents of thermoplastics, and (5) volatilization of low boiling temperature compounds may take place and hence special precaution is required.

In the organic polymer solidification method, urea-formaldehyde resin is usually added and thoroughly mixed with the waste. A catalyst is subsequently added to complete the polymerization process. A spongy type of material is formed which entraps the particulate matter and separates the liquid component of the waste. This spongy material may be dried prior to disposal. However, it is often loaded in containers and buried.

The above method can be applied to either dry or liquid wastes and its use usually requires only small amounts of additives. The resulting waste-polymer mixture has a lower bulk density in comparison to the cement-fixed sludges. However, there are some disadvantages: (1) the catalysts added are highly acidic and will leach out any metals contained in the waste, and (2) the waste particles are bound in a loose resin matrix, and some of the organic polymers are biodegradable.

Encapsulation is usually referred to as a process in which the waste particles are coated with a binding material. The most commonly used process for sludges involves the use of a polybutadiene binder. This is followed by the application of a thin polyethylene jacket by mechanical means around the polybutadiene impregnated sludge to form an encapsulated block, which is disposed of. This process provides an impervious and chemically inert barrier between the sludge constituents and the environment, and hence even very soluble constitutents can be contained. The process requires skilled labor and specialized equipment. Also, heat is required to form a thermoplastic. Some type of jackets are flammable. The materials used are often expensive and the waste sludge has to be dried before it is encapsulated.

Solidification and encapsulation processes have been used successfully for many industrial waste residuals containing potentially hazardous organics. These processes are evaluated primarily on the basis of leachability and strength of the solidified or encapsulated material. A number of proprietary processes have been reported to stabilize sludges from industries such as paint, tannery, pharmaceutical, PCB, chemical, electronic component manufacturing, and oil refinery wastes. These sludges are known to contain potentially hazardous organic compounds.[34] These proprietary processes all claim a low rate of leachability of the solidified wastes. Leachability of inorganics is reported to be low from these wastes when they are properly stabilized/solidified. No information on the leachability of organics from the solidified wastes is available. Based on the low leachability of inorganics, a low degree of leachability of organics may also be expected because of the impervious nature and resistance of the materials used for solidification and encapsulation.

Techniques such as ultrafiltration, solvent extraction, carbon adsorption, resin adsorption, steam stripping and air stripping may be applied to industrial wastes for the removal of organics contained in the aqueous fraction, and for the reduction of the quantity of these organics adsorbed onto the solid fraction. The removal of such organics by pretreatment may also permit the biological stabilization of the industrial wastes. Although these techniques are developed, they have not been used commonly in industrial sludge treatment.[26]

Certain organic liquid wastes may be detoxified and rendered non-hazardous by processes such as chlorinolysis and microwave bombardment. Chlorinolysis can be termed as a manufacturing process instead of a waste treatment process because carbon tetrachloride is produced from waste chlorinated hydrocarbons. The waste chlorinated hydrocarbons are made to react with excess chlorine at a temperature of about 500°C and a pressure of about 200 atmospheres.[26]

The detoxification of hazardous organic wastes may be accomplished by microwave disharge treatment. An assessment of this technology which may be applied to small quantities of highly toxic materials which cannot be handled by any other means is being made by the Lockheed Company. Organophosphorus pesticides, chemical warfare agents, organonitrogen compounds wastes that are potential carcinogens and teratogens, and halogenated hydrocarbons and related pollutants are reported to be amenable to treatment by this method.[35,36] This technology is not in wide use and little information is available on its application to industrial organic sludges. However, data reported from laboratory experiments utilizing oxygen plasmas and pure substrates have shown that the treatment of hazardous organics by microwave discharge was successful.[35,36] Table 27 shows the degradation products reported for specific wastes tested.

Thermal destruction processes such as incineration are well established. The fluidized bed type of incineration process offers great promise for the destruction of hazardous wastes and has been investigated with several types of wastes. Another thermal process known as calcination is also well established for the treatment of industrial wastes. This process can handle complex wastes containing both inorganic and organic constituents. The organics are destroyed at about 1000°C, and a sintered solid mass is formed as an end product. This process is likely to emerge as a practicable process particularly for the processing of tars, sludges and other residuals whose disposal poses a difficult problem.

Other methods for the treatment of hazardous organic residuals have been described such as molten salt combustion for the degradation of PCBs, UV radiation for the degradation of PCBs and kepone, and degradation of complex organic structures by ozone and chemicals such as chloroiodides.[37]

Performance of Current Systems - Overview

The general operating and performance characteristics of various thickening and dewatering equipment have been summarized in Table 20.

Very little is known on the effect of conditioning on the organics contained in the sludges or how the contained organics affect the performance of a conditioning technique. However, it can be assumed that techniques involving heat are likely to volatilize some sludge organics. Dewatering techniques which remove progressively more quantities of water would also remove greater quantities of water-soluble organics.

Biodegradable sludges may be thickened and digested either aerobically or anaerobically in order to stabilize them prior to their disposal on land. The degree of stabilization of a biodegradable sludge by these methods can be measured by the extent of destruction in its volatile solids content. Depending on the loading rate, temperature and detention time employed in the process, about 25 to 50% of the initial volatile solids content may be destroyed. Non-hazardous industrial wastes such as those from food and vegetable processing industries are stabilized generally by digestion. Where industries discharge their wastes to municipal systems, the sludge solids resulting from the industrial waste are digested along with those contributed by the sanitary wastes. The performance of such systems generally parallels those processing municipal wastewater primarily.

In aerobic stabilization processes, biodegradable organic compounds are oxidized to CO_2 or utilized in the synthesis of new cells. In the anaerobic digestion process, the end products are methane and CO_2. In addition, volatile fatty acids and unused substrate may also be present if digestion is not completed. Toxic industrial organics may inhibit the digestion process. Laboratory studies have shown that acrylonitrile, at 5 mg/L, carbon tetrachloride, at 10 mg/L, and 1,2-dichloroethane, at <1 mg/L, were toxic for the anaerobic digestion process.[38] Several aromatic compounds have also been reported to be resistant to aerobic digestion. It has been found that the presence of two or more hydroxyl groups on the benzene ring increased the resistance of the compound to biological oxidation. Progressive addition of nitro groups on an aromatic ring increased recalcitrance of the aromatic compounds to microbial degradation. The presence of chloro, methoxy, or phenoxy groups on the ring also increased resistance toward microbial degradation. However, there are microorganisms that can degrade partially some of the normally

Table 27. Degradation Products Formed by Microwave Detoxification of Selected Wastes

Pesticide/Wastes	Conversion	Reaction Products
Malathion "Cythion" ULV	>99.98	SO_2, CO_2, CO, H_2O, HPO_3 or H_3PO_4.
PCB Aroclor, 1242	>99.9	CO_2, CO, H_2O (Cl_2O, $COCl_2$)
Methyl Bromide	99	CO_2, CO, H_2O, Br_2, BrO_2.
Phenylmercuric acetate "Tyrosan" PMA - 30	99.9	Hg, CO_2, CO, H_2O.

recalcitrant compounds. A list of these organisms and the substrates they oxidize is summarized in a recently published report.[39]

As indicated earlier, composting of oily wastes and explosive wastes which contain hazardous organic substances was at least partially effective. It has been reported that land treatment and disposal has been used for non-hazardous organic wastes and some industrial wastes containing hazardous organics such as pulp and paper mill sludges, iron and steelmill sludges, and pesticide manufacturing wastes.[40] The performance of a landfill disposal system for hazardous wastes and sludges depends primarily on the criteria used in their design and on climatological and characteristics of the soil, nature of the waste applied, and the operational practice employed.

The performance of incinerator systems may be judged on the basis of the following: (1) ability to process a given type of waste, e.g., plastic, wood, or other high moisture residuals, (2) ability to comply with the local air pollution ordinances, (3) capital and operating costs, (4) disposal capacity, i.e., pounds of waste processed/ft^2 of incinerator bed area/time, (5) ease of removal of ash, and (6) ease of operation and maintenance. The performance characteristics of several incineration systems for treating various types of industrial waste sludges have already been presented.

Incineration converts the carbonaceous fraction of the sludges primarily to CO_2. If the oxidation is not complete, some CO may be found. Other gaseous emissions of incineration may include oxides of nitrogen, SO_2, and halogens depending on the original characteristics of the sludge. If nickel is found in sludges, the stack emissions may include nickel carbonyl, which is toxic.

Information on performance of other non-conventional processes cited earlier for the treatment of industrial sludges is meager. Methods such as distillation can be applied economically for reclaiming waste oils, but it cannot be applied for the treatment of sludges or slurries. Evaporation may be effective for both aqueous wastes and sludge suspensions. Dilute pesticide wastes, TNT wastes, paper mill wastes, molasses wastes, and distillery wastes may be effectively evaporated in ponds. Multiple stage evaporation techniques using solvent extraction of sludges may be effectively used for the production of a very dry sludge as was demonstrated with pet food and pharmaceutical waste sludges.[25]

The performance of various stabilization/solidification and encapsulation techniques appears to be quite satisfactory for processing PCB and pharmaceutical residuals in terms of the formation of a product which will produce no leachate.[33]

The performance of land disposal systems may be optimized by assuring that applications of industrial waste residuals are compatible with characteristics of the landfill site. In order to achieve this objective, both landfill sites and wastes are classified by the State of California and guidelines are prescribed for matching residuals with the landfill sites.

In this classification of landfill sites, a Class I or Secured Landfill facility cannot discharge to usable waters and hence can receive all types of residuals. An aquifer must be separated from the disposal bed by an impervious geological formation and the site must be protected against flooding and washout. A limited Class I site, in contrast to the Class I sites which receive all types of wastes, places restrictions on the types and amount of waste it receives due to the possibility of flooding.

A Class II-1 Landfill type of facility can be located without severe restrictions regarding aquifers. If natural geological conditions do not protect against the movement of contaminants of applied sludges, such protection may be achieved by containment of wastes by use of artificial barriers. Non-water soluble and non-decomposable solids, and wastes containing chemically or biologically decomposing materials that will not impair the quality of ground water are accepted at these sites. Some toxic wastes may also be accepted.

A Class II-2 Landfill is a disposal site where a vertical and lateral continuity or movement of the disposed residuals is permitted with usable groundwater. Nevertheless, some protection is usually ensured due to naturally occurring hydrogeologic features of the site.

Class III Landfill sites are disposal areas that provide no protection for groundwater quality. Wastes when disposed in such sites may reach the groundwater. Only wastes which are not soluble in water and inert solids may be disposed of in such sites.

As can be seen from the above classification, secured landfills are preferred for the disposal of sludges containing hazardous organics, to ensure adequate environmental protection. Performance of surface impoundments where liquid wastes or slurries are contained may be improved by constructing them either in hydrogeologically safe areas, or by installing impervious liners prior to introduction of wastes into them. In addition, a free board of 2 ft or greater should also be provided to avoid flooding of the neighboring terrain.

Economics

The economics of industrial residual treatment and disposal is a complex subject. The costs are a function of several factors including, (1) nature of the waste, (2) considerations such as on-site vs. off-site disposal, (3) transportation distance, (4) disposal site location and site preparation costs, (5) pretreatment or modification of waste to render it suitable for disposal, e.g., encapsulation, chemical fixation, detoxification, etc., (6) supplemental fuel for incineration, (7) cost recovered from reclaimable materials, and (8) monitoring costs, etc.

A recent report from the Illinois Institute of Natural Resources summarized the cost estimates published by USEPA in 1978 for various methods of disposal: (a) secured chemical landfill, \$30-55/ton, (1.5-2.75¢/lb), (b) incinerator, \$75-265/ton, (3.75-13.25¢/lb), (c) landspreading, \$2-25/ton (0.1-1.25¢/lb), (d) chemical fixation, \$10-30/ton (0.5-1.5¢/lb). For purposes of comparison, this report presented the costs published by the Manufacturing Chemists Association (MCA) in 1979 for off-site disposal excluding pretreatment and transportation costs: (a) incineration, 1-8¢/lb, (b) chemical landfill, 0.2-4¢/lb, (c) deep-well, 1.8-3¢/lb, and (d) sanitary landfill, 0.8-1.5¢/lb. The MCA reported that transportation costs vary between 0.6-3.2¢/lb within a radius of 600 miles from the waste generation site.[1]

Some of the above costs compare favorably with those published for Allegheny County in Pennsylvania where costs were based on actual monitoring of the expenses incurred. These are given in Table 28.[28]

The following benefits are anticipated when the regulatory program of RCRA goes into effect: (1) reduction of groundwater pollution caused by leaching of toxic

Table 28. Net Unit Costs of Disposal of Industrial and Municipal Residuals Allegheny County, Pa.[28]

Type	Unit Cost
Oil Reclamation	2.7 ¢/lb.
Solvent Recovery	67 ¢/gal.
Industrial Organic Sludge (disposed to Wastewater Treatment Plant)	0.2 ¢/lb.
Municipal Organic Sludge	0.2 ¢/lb.
Scientific Landfill	2.6 ¢/lb.
Sanitary Landfill	0.16 ¢/lb.
Incinerator	0.08 ¢/lb.

pollutants from improperly designed and operated landfills and impoundments, (2) reduction in poisoning and injury due to direct contact with toxic pollutants contained in wastes and sludges, (3) reduction in pollution of surface waters from hazardous wastes stored or disposed of in field and river banks, (4) reduction in illicit dumping of hazardous wastes in soil and water environment, (5) abatement of air pollution from poorly operated incinerators, (6) reduction in mishaps at hazardous waste disposal sites due to improved training of personnel and management of disposal sites, (7) prevention of accidents and mishaps in communities located near disposal sites as a result of quick implementation of contingency plans, and (8) reduction in future adverse impacts due to decontamination or other secured measures taken at the time of closure of a disposal site.[41]

Although the expected improvements are not quantifiable, it is expected that they will be substantial. In addition, costs that have hitherto been borne mainly by the public for environmental clean-up necessitated by improper, surreptitious disposal of industrial residuals, will in the future be borne by the responsible party.

The implementation of RCRA regulations hopefully will force industries to comply with such regulations for hazardous waste management, thereby minimizing the possibility of repetition of incidents similar to the Love Canal episode.

A detailed account of the impact of RCRA on a national level is beyond the scope of this paper. However, based on certain assumptions, the USEPA predicts that the implementation of RCRA will have a broad impact on industry while deriving the potential benefits listed above.

In 1980, RCRA will affect about 67,000 hazardous waste generators producing approximately 41 million metric tons of hazardous waste annually. A major portion of this waste is generated by the chemical and allied industries. In a study covering 29,000 hazardous waste generators which produced 13.7 million metric tons of hazardous waste in 1978, the USEPA predicted that they will incur an incremental cost of $510 million/year for hazardous waste treatment and disposal. This cost was stated to be less than 0.2% of the receipts on marketed goods. According to the EPA, six major industrial categories will be significantly affected in terms of potential closure, loss in jobs, and possible price increases. These are (1) textiles, (2) leather tanning, (3) electroplating, (4) inorganic chemicals, (5) organic chemicals, and (6) non-ferrous smelting and refining. Of these, textile mills and organic chemical industries are known to generate sludges containing toxic organics. Some plant closures are also possible in segments of the explosives, petroleum re-refining, pharmaceuticals, and plastics industries as a result of the difficulty that may be experienced in complying to the RCRA regulations. All of these industries generate sludges containing toxic organics.

At the state and local level, the impact of the implementation of RCRA will also be felt eventually. An immediate effect will be the implementation of a manifest system for identifying and accounting for the hazardous waste generated in various industries including the method of disposal. If the manifest system is strictly enforced it should reduce illegal dumping of hazardous wastes and sludges on open sites and in local sewers. However, if it is poorly managed, it could result in more illegal dumping than at present. The RCRA will require careful monitoring of existing hazardous disposal sites. This will possibly decrease the number of available hazardous disposal sites and will increase the disposal costs. Unfortunately, many small municipalities neither have the financial resources nor the administrative and technical manpower to implement their manifest system properly and consequently will continue to encounter illegal dumping of wastes and sludges into their sewerage systems.

As a guard against illegal dumping and to comply with the NPDES permit restrictions at a local level, the Metropolitan Sanitary District of Greater Chicago has implemented its own manifest system, and an evaluation of the performance of this program over a year revealed that <1% of the industries, (117 industries), violated the requirements for reporting the amount of waste generated on their premises. It is hoped that even tnese industries like all others will comply with the MSDGC manifest requirements in the future.

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